METALLURGY

GREGORY

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To Julius Kayser, Esq.,

*this book is respectfully dedicated in appreciation
of his kindness and encouragement during a very
critical period in the author's life.*

INTRODUCTION

By PROFESSOR C. H. DESCH, F.R.S.

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The need of some metallurgical knowledge on the part of the engineer becomes more evident each year, as the metals and alloys used in engineering construction become more numerous and more varied, and as the conditions under which they are employed become more onerous. Not so many years ago mild steel, wrought iron, and cast iron, with a few non-ferrous alloys, were all that were required, but a far wider field is needed at the present day. The aeroplane and automobile industries have been largely responsible for the development of metals having a high resistance to fatigue, whilst the needs of the chemical industry have had to be met by the production of alloys which retain a large part of their strength at elevated temperatures, leading in turn to the construction of steam boilers for use at high pressures and temperatures. The attempt to lessen losses by corrosion has brought about the invention of many alloys, ferrous and non-ferrous, which are highly resistant to atmospheric corrosion and to attack by such agents as sea-water.

These newer materials have as a rule to be subjected to heat-treatment before use, and unless the best treatment be applied, the metal cannot develop the full qualities which distinguish it from other and less costly varieties. Some knowledge of the effects of heat-treatment is therefore essential to the engineer, and this involves a study of the means, such as microscopical examination, by which the correctness of the treatment may be determined.

For the recognition of flaws and defects there is no substitute for experience, but the student of engineering can, by the study of a suitable textbook, be put in the way of understanding the appearances presented by fractures and injured parts. An acquaintance with the internal structure of metals is required for this purpose also.

The experience gained by Mr. Gregory in the works as well as in the teaching of metallurgical students has been assisted by contact over a series of years with a class for aeronautical inspectors held annually in Sheffield. The construction of aircraft brings to the notice of the engineer most of the problems connected with the use of modern materials under the most severe conditions, and the metallurgist realizes, perhaps better than in relation to any other industry, the nature of the questions to which the engineer seeks an answer. The present work is intended to supplement, not to replace, practical experience, and it is to be hoped that it will be the means of inducing many engineers to study the materials which they handle, and also of bringing about that closer contact between engineers and metallurgists which is so desirable in the interests of industry.

September, 1931.

PREFACE

The writing of a simple textbook of general metallurgy has its own peculiar difficulties. It is clearly impossible to deal exhaustively with the whole subject of both ferrous and non-ferrous metallurgy in a volume of less than 300 pages. The aim, therefore, has been to provide an introduction to the study of metallurgy useful not only to engineers, for whom the book is primarily written, but to all those interested in this important branch of applied science. If this hope is fulfilled, and the reader encouraged to consult more specialized works of reference, the author will feel that his labour has not been in vain.

The book has been roughly divided into two parts. The first part deals with the metallurgy of iron and steel, whilst the later chapters are devoted to the study of the non-ferrous metals and alloys. To the beginner the necessity for a thorough understanding of the principles dealt with in Chapter III cannot be too strongly emphasized.

Frequent reference has been made to various journals and papers; and in particular, to the publications of the Iron and Steel Institute, the Institute of Metals, and the Mond Nickel Co., Ltd. Special acknowledgment is due to the last-named for the loan of blocks for figs. 129 and 131.

The author is indebted to Mr. F. Clements, M.Inst.C.E., M.I.M.E., A.M.I.E.E., and the Council of the Iron and Steel Institute for permission to reproduce the blast-furnace diagram shown facing page 4. Thanks are due to Messrs. C. C. Hodgson and P. B. Henshaw for several photomicrographs, and to the last-named gentleman for permission to reproduce the curves given

in figs. 168 and 170. The author is greatly indebted to Mr. G. Glenn for much of the information and several illustrations given in the section on the cold-working of steel.

Most of the photographs were taken in the Metallurgical Department of the University of Sheffield, and in this connexion useful assistance was willingly given by Mr. G. A. de Belin.

The author gratefully acknowledges the great help he has received from Professor Desch, whose kindly interest has been a constant source of encouragement; and to his editor, Professor R. M. Caven, D.Sc., F.I.C., his warmest thanks are due for many helpful suggestions and criticisms. He is deeply indebted to his senior colleague, Mr. J. H. Wreaks, B.Met., whose help throughout the preparation of the whole of the text has been invaluable, and who kindly placed his splendid collection of micro-sections at the author's disposal.

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An attempt has been made to give the source of all information used in the text; but if due acknowledgment has not been made, the author tenders his sincere apologies to the individuals or authorities concerned.

<div align="right">EDWIN GREGORY.</div>

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LIST OF ABBREVIATIONS AND GLOSSARY OF TERMS USED IN THE TEXT

ELEMENTS AND THEIR SYMBOLS

Aluminium	Al	Molybdenum	Mo
Antimony	Sb	Nickel	Ni
Arsenic	As	Nitrogen	N
Bismuth	Bi	Oxygen	O
Carbon	C	Phosphorus	P
Chromium	Cr	Silicon	Si
Cobalt	Co	Sulphur	S
Copper	Cu	Tin	Sn
Iron	Fe	Titanium	Ti
Lead	Pb	Tungsten	W
Magnesium	Mg	Vanadium	V
Manganese	Mn	Zinc	Zn

ABBREVIATIONS EMPLOYED IN HEAT-TREATMENT

N. = normalized.
Ann. = annealed.
W.Q. = quenched in water.
O.Q. = quenched in oil.
Td. = tempered.
A.C. = cooled in air.

ABBREVIATIONS AND TERMS USED IN QUOTING MECHANICAL TEST RESULTS

Y.P. = Yield-point, i.e. the stress in tons per square inch calculated on the original cross-sectional area of a tensile test-piece at which a further small increase in the load produces a sudden extension.

M.S. = Maximum stress, i.e. the greatest load carried by a test-piece during a tensile test, also expressed in tons per square inch calculated on the original cross-sectional area.

Elong. = Elongation per cent, i.e. the actual extension of a predetermined gauge length (generally 2″) expressed as a percentage of this length.

Red. of A. = Reduction of area per cent, i.e. the diminution in area at or near the point of fracture expressed as a percentage of the original cross-sectional area.

B.No. = Brinell number, i.e. the load divided by the spherical area of the inden-
tation produced in the material after the load has been applied to a hardened
steel ball in contact with it. For the testing of steels the standard load is 3000
kilograms applied to a ball 10 mm. in diameter. For most non-ferrous metals
and alloys the standard load is 500 kilograms.

If either the load (L) or the diameter (D) of the ball is varied, correlated
values are only obtained if the ratio L/D^2 is kept constant.

Vickers Hardness numerals are independent of the load, since a diamond
pyramid is employed as the indenting tool.

METALLURGY

CHAPTER I

Iron

Pure iron is not found in nature but, with the exception of meteorites, which are alloys of iron and nickel almost devoid of carbon, always exists in combination with non-metallic elements in forms which are very widely distributed.

Ores of Iron.

Many iron ores cannot be worked profitably on account of their low iron content. Others contain far too large a proportion of other elements, notably sulphur, to be of any value for the extraction of the metal.

The most useful ores are the oxides, hydrated oxides, and carbonates, none of which, however, occur in abundance in the pure state, for they are generally associated with earthy and other foreign matters known as " gangue ". Many ores are smelted in the blast-furnace without any preliminary treatment, but some are subjected to an operation whereby most of the gangue is got rid of and the ores concentrated.

The richest ores are the *magnetites*, mined in large quantities in Sweden. Swedish ores have long been famed for their exceptional purity, particularly those of the Dannemora, Striberg, and Persberg districts. These may contain as much as 66 per cent of metallic iron, but very little phosphorus, and they are used for the production of the finest qualities of Swedish wrought iron.

Pure magnetite has the formula Fe_3O_4, and often exhibits magnetic polarity; hence the name given to it. Even when not

naturally magnetized, it is always attracted by a magnet, and advantage is taken of this property in separating the ore, as mined, from the foreign matter associated with it.

The best kinds contain only small amounts of phosphorus, and although the sulphur content may be rather high, this element is reduced to little more than traces by subjecting the ores to a roasting or calcining treatment. Sulphur, existing as iron pyrites (FeS_2), is evolved as sulphur dioxide (SO_2), and much of what remains is afterwards eliminated by exposing the calcined ore to the action of rain and snow, which washes out soluble sulphates. This latter change is known as *weathering*.

Swedish blast-furnaces, in which the iron is reduced to the metallic condition, are of relatively small capacity, and charcoal is used as the fuel.

Iron ores which when pure approximate to the composition Fe_2O_3 are known as *hematites*, the most important being found in the Cumberland and Bilbao (Spain) districts.

Red hematite frequently occurs in kidney-shaped masses which, on fracture, show a radiating structure.

The best hematites are low in sulphur and phosphorus, and contain up to 60 per cent of metallic iron.

Hydrated oxides, of which the most important are the *limonites* or *brown hematites*, occur in beds in Northamptonshire and Lincolnshire. These ores are usually calcined in order to bring about concentration by driving off combined water, carbon dioxide, and sulphur.

The purest forms of carbonate of iron are ferrous carbonate, $FeCO_3$, and are known as *spathic iron ores*. The lower layers of the Northants deposits are essentially carbonate ores.

Of the impure carbonates, those of chief importance are: *clay ironstones*, found in South Wales, Staffordshire, and West Yorks, in which the iron carbonate is associated with about 15 per cent of clayey matter; and Cleveland ironstones, which are considerably more impure and are smelted with imported ores of higher manganese content.

These ores contain about 33 per cent of metallic iron, but the gangue consists of clayey matter associated with carbonates of lime and magnesia in sufficient quantities to render the ores almost " self-fluxing ", whereby a great economy in limestone is effected. Calcination is generally carried out to remove carbon dioxide and bring about the desired concentration.

Of the foreign ores, those of the greatest importance are found in the Lake Superior district in America and in the Lorraine-Luxemburg district.

The chief American ores are hematites, which are all more or less hydrated. The metallic iron contents vary considerably, but the average value, as mined, is about 45 per cent. These ores are characterized by low phosphorus and high sulphur contents, and, in addition, nearly always contain some copper. Copper is therefore found in the steels produced from the resulting pig-irons; and although small amounts of the element are rather beneficial than otherwise, copper is to be regarded as an accidental impurity in such materials.

The Lorraine-Luxemburg district is one of the largest iron-ore fields in the world, and is the principal source of supply for the German iron and steel industry. The ores are essentially hydrated hematites, and are highly phosphoric. They contain low silica and fairly high lime, and are particularly suitable for the production of pig-irons which are to be used in basic steel-making processes.

Typical compositions of different ores are given in the following table:

	Good Magnetite (Swedish) 1.	Good Red Hematite (Cumberland) 2.	Calcareous Brown Hematite (Lincolnshire) 3.	Eston Block Ironstone (Cleveland) 4.
Fe_2O_3	68·04	74·23	47·14	2·13
FeO	21·37	—	—	37·96
MnO	1·40	0·28	1·72	0·69
Al_2O_3	3·42	6·61	4·08	8·82
CaO	0·20	1·02	11·45	5·51
MgO	1·18	0·01	2·97	3·73
SiO_2	2·60	8·62	11·95	9·11
P_2O_5	0·01	0·02	0·87	1·32
SO_3	0·01	0·02	0·10	(S.) 0·056
H_2O	1·77	8·43	12·40 ⎫	30·75
CO_2	—	0·79	6·87 ⎭	
Metallic iron ..	64·25	51·96	32·99	30·92
			Fe (calcined)	42·14
			Fe (dry)	33·10

1 and 2. J. O. Arnold.

3. Report on Sources and Production of Iron and other Metalliferous Ores. (Dept. of Scientific and Industrial Research, 1918.)

4. Bolckow, Vaughan & Co., Ltd.

The Metallurgy of Iron.

There are three commercial kinds of iron: cast or pig-iron, wrought iron, and steel.

Pig-iron is made from iron ore in the blast-furnace, and when pig-iron has been simply remelted it is known as cast iron. Cast iron is the most impure kind of iron. Its special properties, however, depend on the carbon it contains, combined or uncombined, and on smaller proportions of other elements derived from the ore.

Wrought iron is made from pig-iron by processes which considerably reduce the proportion of impurities; and its special properties depend on the mode of manufacture.

Steel, which is made in a variety of ways, contains a proportion of carbon generally greater than that of wrought iron; in fact, carbon may be regarded as an impurity in wrought iron, but is an essential constituent in steel. Unlike wrought iron, most steels are cast, and many valuable properties are induced in them by the introduction of other elements in large or small amounts.

The Blast-furnace.

The blast-furnace, in which the iron is reduced to the metallic condition, is so named because the chemical changes within it depend on the introduction of a blast of air. It is essentially a large cylindrical steel vessel, lined with firebrick and tapering considerably towards the lower end. The top is closed by a cup and cone arrangement, (as shown in the plate) and serves for the introduction of the charge, consisting of iron ore, limestone, and coke.

In some cases, the air blast is cold when it enters the furnace, but it is more often preheated in stoves which are heated by the combustion of a part of the waste gases from the furnace. At least two stoves are used for each furnace, the air being preheated in one whilst the burning gases are heating up the other stove. At regular intervals, the direction of the blast is reversed, and by this means some uniformity in the temperature of the air entering the furnace is obtained. This temperature is generally between 550° and 750° C.

The blast enters through water-cooled pipes or *twyers*, and the pressure varies between 5 and 15 lb. per square inch, according to the capacity of the furnace.

The waste gases, which still contain a considerable proportion of combustible matter even after passing through the stoves, are utilized in raising steam for the blowing engines and for the production of electrical energy. These gases, which contain large

quantities of dust, are also cleaned and then used in gas engines, or in some cases for the blowing engines themselves.

Chemical Changes in the Blast-furnace.

The carbon in the fuel combines with the oxygen of the air blown in to form carbon dioxide (CO_2), but this gas almost immediately either dissociates or combines with more carbon to yield carbon monoxide (CO), thus:

$$CO_2 + C = 2CO.$$

The carbon monoxide then passes up the furnace chamber and brings about reduction of the iron according to the reaction:

$$Fe_2O_3 + 3CO = 2Fe + 3CO_2.$$
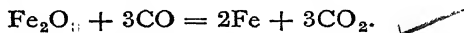
At first sight, therefore, the reduction of iron oxide appears to be a very simple operation. Actually, however, it is not quite so simple owing to the reversibility of the above reactions, which are therefore greatly influenced by temperature and pressure variations, so that the effective blast-furnace operations really take place between comparatively narrow limits only.

As the charge descends, reduction of other oxides in the ore takes place, and any silicon, manganese, and phosphorus thus liberated dissolve in the molten iron.

The extent to which these reductions occur depends on the composition of the charge, the temperature of the furnace, and the " burden " of the furnace, i.e. the ratio of ore to fuel. With a heavy burden, when the atmosphere in the furnace is not sufficiently reducing in character, comparatively little reduction of these other substances occurs, with the consequent production of low silicon pig-irons.

On the other hand, a light burden may yield irons containing as much as 4 or 5 per cent silicon. Reduction of silica is promoted by metallic iron, and a high temperature also favours the production of high silicon irons.

Sulphur combines with the lime to form calcium sulphide which dissolves in the molten slag. In this case also, strong reducing conditions are necessary, and consequently the irons which are richest in silicon are, in general, the lowest in sulphur.

The temperature at which reduction of the iron oxide occurs

is comparatively low—about 400° or 500° C., but as the spongy mass of iron so formed descends, it takes up from 5 to 6 per cent of impurities, chiefly carbon. Later on the metal melts, and, when it sinks to the bottom or hearth of the furnace, is in a perfectly fluid condition.

The limestone also suffers decomposition, the liberated lime then combining with the silica of the gangue to form a fusible silicate or *slag* in which other non-metallic substances are dissolved. The slag floats on the surface of the heavier metal.

When the slag level attains a convenient height, which must obviously be below the twyers, the excess flows away through a " cinder " hole provided; and when sufficient metal has collected, it is allowed to flow into previously prepared sand or " pig " beds by driving an iron bar through a clay plug made low down in the furnace hearth.

After cooling, the harder varieties of slag are broken up and used in road-making, whilst large quantities are granulated and used in the manufacture of synthetic cement.

The *pig-iron* obtained is allowed to cool, and is then broken into short lengths known as pigs, either by hand or with the aid of mechanical " pig-breakers ".

Pig-iron Fractures.

The appearance of the fractured pig-iron is governed chiefly by its composition, but is also dependent on the rate at which the metal cools.

In the presence of much silicon, the carbon in the solid pig-iron exists mainly in the form of flakes of " free " carbon or *graphite*, which, together with the metallic iron, give rise to a characteristic *grey* fracture.

When the iron contains very little silicon, and has been cooled fairly quickly from a high temperature, practically the whole of the carbon is retained in chemical combination with the iron as carbide of iron, Fe_3C. This compound also exhibits a metallic appearance, and the fractures of the pig-irons are then quite *white.*

Sulphur inhibits the decomposition of carbide of iron; high sulphur therefore tends to produce white irons.

The main object of the high silicon in pig-iron is the consequent lowering of the sulphur content, with the result that, in general, grey irons contain little sulphur.
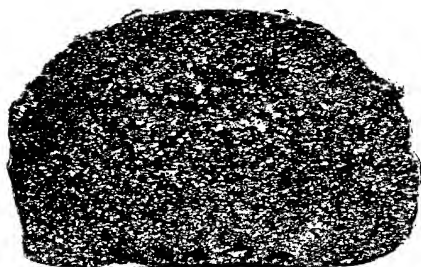
'Open' Grey Iron

Mottled Iron
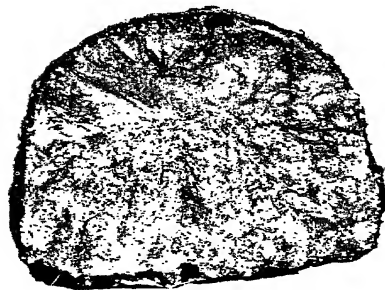
White Iron

Fig. 1.—Showing typical pig-iron fractures

In many medium silicon pig-irons about one-half the total carbon is in the form of graphite, the remainder being combined with the iron. In such irons, graphitization commences from a series of centres, and the graphite then exists in star-shaped masses which give rise to characteristic *mottled* fractures.

Typical fractures are shown in fig. 1.

Phosphates are almost entirely reduced, and the resulting phosphorus dissolves in the molten iron as phosphide of iron, Fe_3P; the phosphorus content of pig-iron is therefore entirely dependent on the raw materials used.

Phosphorus has no influence on the greyness of the fracture of pig-iron.

The texture or " closeness " of the grain is often taken as a guide to the suitability of the iron for certain specific purposes.

Close-grained irons are characterized by extremely small graphite plates, the sizes of which are determined chiefly by the compositions of the irons and the rate of cooling.

The irons produced by smelting phosphoric iron ores, and therefore containing large quantities of phosphorus, are usually grey and contain much silicon. Phosphorus is soluble in solid iron to the extent of about 1·4 per cent at high temperatures, but this solubility is greatly decreased by the presence of carbon. The excess then forms Fe_3P, which, together with carbide of iron and the foregoing solid solution, gives rise to the formation of a ternary compound with a melting-point as low as 952° C. Many of these irons, therefore, are used in the manufacture of thin castings of intricate design, since the phosphorus confers a greater degree of fluidity at lower temperatures.

Compositions of Pig-irons.

The compositions of some typical pig-irons are given in the following tables, together with certain purposes for which these irons are used.

SEATON CAREW CO.'S IRONS (EAST COAST)

		C.C.	Gr.	Si.	S.	P.	Mn.
No. 1 ..	..	0·30	3·73	2·50	0·02	0·05	1·00
No. 2 ..	..	0·45	3·53	2·25	0·03	0·05	1·00
No. 3 ..	..	0·56	3·18	2·00	0·04	0·05	1·00
No. 4 ..	..	1·00	2·75	1·50	0·10	0·05	1·00
No. 5 ..	..	1·55	2·45	1·00	0·20	0·05	0·75
Mottled	..	2·05	1·50	0·75	0·25	0·05	0·50
White	..	3·15	trace	0·65	0·30	0·05	0·50

CLEVELAND PIG-IRONS (BOLCKOW, VAUGHAN & CO.)

	C.C.	Gr.	Si.	S.	P.	Mn.
No. 1	0·10	3·50	3·42	0·034	1·50	0·67
4/5 per cent Si	0·03	3·10	4·0–5·0	0·040	1·50	0·72
No. 3	0·15	3·45	2·5–3·0	0·050	1·50	0·62
No. 4 Foundry	0·25	3·41	2·38	0·080	1·50	0·55
No. 4 Forge ..	0·32	3·25	1·84	0·120	1·50	0·61
Mottled ..	1·60	1·60	1·32	0·230	1·50	0·59
White ..	3·20	trace	0·46	0·520	1·50	0·54

No. 3 is suitable for thin ornamental castings and hollow ware, either alone or with a little of No. 1.

A mixture of No. 3 with an equal weight of hematite pig-iron is also used for the highest class of engineering castings, for high-pressure cylinders, engine details, &c.

HEMATITE PIG-IRONS

CUMBERLAND IRONS (WEST COAST)

	Comb. Carbon.	Graphite.	Silicon.	Sulph.	Phosph.	Mang.	Uses.
No. 1 Bessemer	0·5	3·5	2·0–3·0	0·01	·02—·05	·1—·3	Acid steel manufacture, ingot moulds, annealing boxes, &c.
No. 2 ,,	0·6	3·3	2·0–2·5	·02	·02—·05	·1—·3	
No. 3 ,,	0·8	3·1	1·5–2·0	·04	·02—·05	·1—·3	
Foundry No. 3	0·9	2·8	2·0–2·5	·05	·02—·05	·1—·3	Strong castings or for diluting inferior irons, ingot moulds.
Forge No. 4	1·1	2·5	1·5	·08	·02—·05	·1—·3	In puddling for the production of superior wrought iron.
Forge No. 5	1·3	2·1	1·2	·11	·02—·05	·1—·3	Ornamental castings where little strength is required.
Mottled iron	1·8	1·4	·7	·15	·02—·05	·1—·3	
White iron	3·0	trace	·3	·20	·02—·05	·1—·3	Basic open hearth steel-making in limited amounts only.

The numbering of the pig-irons is purely arbitrary, but in general, as the number of the iron increases, the silicon decreases, but the sulphur increases, and is highest in the white irons.

Swedish irons are exceptional in this last respect, owing to the facts that the ores are exceptionally pure and charcoal is used as the fuel in the blast-furnace.

ANALYSES OF SWEDISH PIG-IRONS

	C.C.	Gr.	Si.	Mn.	S.	P.
Grey ..	0·40	3·60	1·10	0·35	0·020	0·030
Mottled	2·00	2·00	0·60	0·40	0·015	0·025
White	3·50	0·40	0·20	0·40	0·020	0·020

Cast Iron and Iron Castings

Large quantities of pig-iron are simply remelted and used for the production of castings, the composition of the resulting cast iron being obtained by blending various brands.

Melting is usually carried out in what is really a small blast-furnace but is known as a *cupola*, into which is charged a mixture of pig-iron, limestone, and coke.

The air-blast enters through twyers situated in the lower part of the cupola, and is generally not preheated, although the use of the hot-blast is coming into more general use.

During melting, some oxidation of silicon and manganese occurs, always accompanied by an increase in the sulphur content, which is greater when inferior coke is used. For these reasons, some of the pig-iron is often remelted in an " air " or reverberatory furnace, the only drawback being that due to the comparatively low temperatures obtainable, with consequent lack of the necessary fluidity. Air-furnace metal is therefore seldom used alone for large castings, but is more often mixed with cupola metal before or whilst being poured into the mould.

Remelting is now also carried out in the basic-lined electric furnace. This is advantageous, because any required degree of fluidity can be obtained, sulphur is removed, and the chemical composition is readily controlled.

Normally, the chemical changes in the cupola are comparatively slight, average figures being as follows:

Silicon—decreased by about 0·25 per cent.
Manganese—decreased by about 0·3 per cent.
Sulphur—increased by about ·015—·03 per cent.
Phosphorus—very small percentage increase due to concentration.

The fluid metal is tapped into refractory-lined bucket-shaped vessels known as *ladles*, from which it is poured either directly, or from smaller hand-ladles known as *shanks*, into sand moulds, the character of which depends on the type of castings required.

The object of the iron-founder is to produce a mass of given shape and size, advantage being taken of the very valuable property of cast iron whereby it expands after freezing, i.e. crystallizing from a state of fusion. This expansion is due to the decomposition of carbide of iron into iron and graphite, a change involving an increase in volume which results in the production of castings taking sharp impressions of the moulds.

The production of sharp castings also depends on the viscosity of the metal, which decreases with increasing casting temperature. There is, of course, a practical limit to the temperatures obtainable, and advantage is taken of the fact that the greater the carbon content of the iron, the greater is the fluidity at a given temperature.

The freezing-point of pure iron is 1535° C., whilst that of an iron containing about 4·3 per cent of carbon is only about 1130° C. Silicon still further lowers the freezing-point, and, as already pointed out, phosphorus will give fluidity at as low a temperature as 952° C.

After solidification, further cooling results in the ordinary normal contraction taking place, with consequent *shrinkage* of the casting as a whole. This shrinkage, which must be allowed for, has been shown by several workers to be dependent on the amount of silicon in the iron. Shrinkage may give rise to the formation of contraction cavities in the solid casting. This is overcome by the use of " risers "—cylindrical apertures intentionally made on top of the mould—which are filled with the molten metal, the latter then serving as a reservoir to fill in any contraction cavity that may be formed in the casting proper.

Moulding Sands.

These are siliceous materials containing a little clayey matter, and they must fulfil certain essential requirements, viz.:

(1) They must be of such a refractory nature as to withstand high temperatures without fusing.

(2) They must possess a certain degree of porosity in order to allow of the free passage of air and gases at the moment of casting.

since otherwise cavities may be formed in the solid metal, which consequently may not take the complete shape of the mould.

(3) The sand should be easily removable from the cold casting, to which it should impart a clean, smooth skin.

The sand forming a mould may be divided into two portions: that forming the face of the mould being described as *facing sand*, whilst that which constitutes the main body or " backing " is known as *floor* or *black sand*. Facing sand is most important where the surface of the casting is concerned, and the general rule is that the more intricate the shape of the casting, the finer must be the state of division of the facing sand.

In modern practice, there are four chief methods of moulding, generally with the use of metal patterns, or, in some cases, no pattern at all.

Green Sand Moulds are made from sand which has been made sufficiently moist to hold together when warmed. The surface of the mould which is to be in contact with the metal is then sometimes dried by means of a flame. This merely dries the " skin ", and such moulds are only suitable for light castings.

Dry Sand Moulds.—In this case the mould after ramming is dried in an oven, and the facing sand is much finer than the backing. Green sand is friable after thorough drying, and for dry sand work the sand is bonded by contained clay. In some cases clay is actually added, and generally its proportion is much higher than in green sand.

Loam Sand Moulds require no patterns, and, although templates may be used, are generally hand-fashioned. For this reason loam sand must obviously be more plastic than ordinary sand, and contain considerably more clayey matter.

Clay may decrease the porosity of the mould, which is therefore improved by mixing some organic matter with the sand; straw, manure, and powdered coal are used for this purpose.

With large castings, the straw serves to hold the sand together, and in most cases the backing sand is rendered more permeable by means of *vent-holes* made by the introduction of wire rods through the sand. These holes must obviously not penetrate too near to the inner surface of the mould.

For cores, a sand of considerable strength is required, since these suffer more handling than the moulds themselves. Sea sand mixed with oil appears to give satisfactory results, and, after drying,

this mixture sets very hard. After casting, the oil burns away, and the sand is then easily shaken out.

The actual surface of a mould is always protected by a thin layer of material known as " blacking ", which prevents the metal from entering the pores in the sand, and thus gives better surfaces to the castings. The substances used are carbonaceous in character, such as powdered coal, blacklead, &c.

Chill Moulds or " permanent " moulds consist entirely of metal, and are used when large numbers of the same type of casting are required.

In the casting of intricate sections of variable thickness there is always a tendency to chill the thinner parts. Unequal contractions may then give rise to unsound material, and surface cracks may develop due to the unequal stresses and strains set up. These effects are largely avoided by the introduction of cast iron or steel bars into the sand near to the thicker sections. These " chills ", as they are called, rapidly conduct the heat from the thicker parts, and thus ensure a more or less even rate of cooling of the whole mass.

The modern method by which cylindrical objects are centrifugally cast merits special mention. For pipe manufacture this process is gradually replacing the older method of moulding and casting upright. The molten iron is allowed to flow into rapidly rotating water-cooled alloy steel moulds; and although at first there was the risk of the production of castings of irregular thickness, this has now been almost entirely overcome.

The chilling effect is very pronounced, and the pipes are therefore annealed in continuous furnaces as soon as they are removed from the moulds.

Effect of Impurities on Cast Iron.

Silicon.—For most purposes, castings are required which show grey fractures throughout. Chilling gives a hard but brittle exterior, most of the carbon being combined, and in the form of " free " carbide of iron, with the production of white fractures.

In grey irons, most of the carbon exists as graphite, and, as with the pig-irons from which they are produced, the fractures are largely controlled by the silicon content. The diagram (fig. 2), due to Maurer, gives some idea of the influence of silicon, but it does not take any account of the size of the casting, and can only be regarded as having a general significance.

A further diagram (fig. 3), due to Greiner and Klingenstein,[*] in which the C + Si content is plotted against thickness, is claimed to be more truly representative. This diagram is for metal having a total carbon content not less than 2·8 per cent.
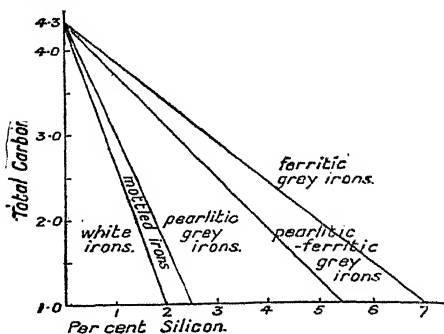
Fig. 2.—Showing Effect of Composition on Fracture of Cast Iron

Grey irons are classified according to their silicon contents. The strength chiefly depends on the size and distribution of the graphite plates, and if curves are plotted showing the relationship
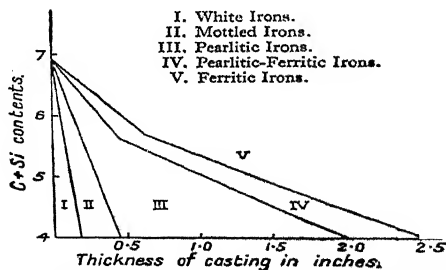
Fig. 3.—Showing Effects of Composition and Dimensions on Cast Iron

between the silicon contents and the crushing, transverse, and hardness values, well-defined maximum values are generally obtained. For compression and hardness, the maxima occur with about 0·8 per cent Si, whilst for transverse tests the maximum

value is obtained with about 1·4 per cent Si. Irons with a higher silicon content—up to 2·5 per cent—are more graphitic in character, and are used for purposes where easy machining is desired.

The general tendency is to give greyer irons with higher silicon and carbon contents. Longmuir gives the following composition as being almost ideal for most general purposes:

Total carbon, 3·0; Si, 1·3–1·5; Mn, 0·7; S, 0·1–0·15; P, 0·5.

Average tests for ordinary grey cast irons are as follows:

	Maximum Stress, tons per sq. in.	Crushing Strength, tons per sq. in.	Transverse Tests, 36″ × 2″ × 1″ bars.
Average	8 to 11	40	28 cwt.
Very good	14 to 16	50	30 to 40 cwt.*
Poor ..	5	30	18 cwt.

Microscopical examination of many grey irons, after etching with a suitable reagent, shows the graphite plates almost completely enveloped by areas of practically pure iron (ferrite), both constituents being the result of the breakdown of the iron carbide (cementite). The structure of such an iron is shown in fig. 4, and the infilling between the ferrite areas consists of alternating plates of soft ferrite and the hard carbide, i.e. a mechanical mixture of definite composition known as pearlite (p. 91), which is much stronger, mechanically, than either the iron or the graphite Under some circumstances, it is possible to obtain structures which show no " free " ferrite, the graphite plates then being embedded in the pearlite matrix (fig. 5).

The " Perlit " process † claims to obtain such structures by careful control of the carbon and silicon contents, together with the use of heated moulds. It is a matter of controversy as to whether the use of hot moulds has any great influence on the production of pearlitic cast irons, and it is thought that the more important consideration is the chemical composition. There seems little doubt, however, that this use does result in a greater uniformity of structure throughout.

Pearlitic irons usually have a comparatively low total carbon content with moderate silicon (1 per cent), together with a fairly high manganese content. The importance of the manganese is not generally appreciated.

The smaller graphite plates and the pearlite matrix result in

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* 0·3″ to 0·4″ deflection at centre.   † British patent No. 210,091.

Fig. 4.—Pearlitic-ferritic cast iron. × 200. Graphite flakes embedded in ferrite (white): dark background is pearlite. Small composite areas are the phosphorus-rich constituent. The stained areas in the ferrite contain manganese sulphide.

Fig. 5.—Pearlitic cast iron. × 250. Shows graphite flakes embedded in pearlite matrix; the large area on the left is the phosphorus-rich constituent referred to on p. 7.

the production of much stronger irons, the tensile strengths of which are in some cases as high as 26 tons per square inch.

In order to increase the strength of cast iron, steel scrap is often charged along with the pig-iron in the cupola. This procedure yields a material with lower total carbon content, and results in the formation of smaller graphite plates. The term *semi-steel* is applied to such mixtures. The term is misleading, as the product is still cast iron in the accepted sense, since the carbon content usually varies between 2·5 and 3·2 per cent.

Semi-steel mixtures are used for heavy castings, hydraulic rams and cylinders, steam hammer and Diesel engine cylinders, &c., and the base is usually a good quality hematite iron. The molten metal is cast hot in order to ensure soundness and freedom from inclusions.

The size of the graphite plates is of great importance in irons for chemical plant, Diesel engine cylinders, &c. If the plates are large in chemical plant irons, the acids penetrate and form crystals of iron salts which may force out the graphite, with the consequence that the surface is rapidly eaten away. In engine cylinders, wear takes place much more evenly if the plates are small.

The distribution of the graphite is best ascertained by micro-examination of the unetched polished sections.

Fig. 6 (*a*) and (*b*) (facing p. 20) are photomicrographs of two samples of cast iron having the following compositions:

	Total Carbon.	C.C.	Si.	Mn.	S.	P.
(*a*)	3·46	0·14	2·44	·76	·057	·71
(*b*)	3·20	0·09	2·66	·35	·101	1·61

These irons were used for glass bottle moulds, (*a*) giving excellent results, whereas (*b*) proved unsatisfactory and "scaled" badly. (*b*) is evidently the composition of a very poor quality iron, but it is also evident that the better heat-resisting properties of (*a*) are associated with the finer graphite plates.

Phosphoric Cast Irons.

These usually exhibit grey fractures and are fairly high in silicon. The low melting-point of the phosphide constituent yields a very fluid iron suitable for the production of sharp castings, and considerable quantities are used for pipes, light engineering castings, stove-grate work, rain-water goods, &c.

Pistons and piston-rings are also made from phosphoric irons.

The phosphide constituent is hard although brittle, and resists wear, and after running for a short time minute channels are formed in the softer ferrite and graphite which maintain oil-films, and thus give rise to a very effective system of lubrication. If the phosphide constituent is at all massive, however, it may chip out and score the cylinder linings.

Sulphur in Cast Iron.

This element is generally regarded as being detrimental to the properties of most castings. One notable exception, however, is that of irons used for the manufacture of " chilled " rolls, where an extremely hard surface to resist wear is desired, such as the rolls used for steel sheets, plates, and strip, and paper and linoleum manufacture.

For these purposes, a low-silicon high-sulphur iron is aimed at, and the effect of the sulphur is of paramount importance, since it increases the depth of chill; this, indeed, is largely controlled by the sulphur content, which is often as high as 0·2 per cent. By carefully controlling the remaining composition, in particular the manganese, which is kept as low as possible, the interior of the roll can be obtained in a comparatively tough grey condition.

White pig-irons are never used for castings, since the molten metal is too viscous and does not give sharp impressions; and, in addition, there is always the possibility of blowhole formation.

Annealing of Castings.

Occasionally, castings are annealed, i.e. heated to a fairly high temperature, and more or less slowly cooled. By these means, cooling-strains after casting are got rid of, and the iron is softened, owing to the further decomposition of carbide of iron into iron and graphite; but the latter then exists as small particles known as " temper carbon ", which does not materially weaken the casting.

Growth of Cast Iron.

Irons containing graphite grow or expand with repeated heat-ings, and in certain cases, to quite a remarkable extent. Since the heating under many circumstances is by no means uniform, this growth may result in buckling and disintegration taking place. It is assumed that the graphite plates swell and then allow of the

easy penetration of gases, whereby oxidation of both silicon and carbon occurs. Carpenter and Rugan * have shown that silicon exerts a marked influence on the growth of cast iron, and in Diesel engine cylinders the proportion of this element is generally kept as low as possible.

According to Piwowarsky,† high silicon irons with large graphite plates also appear to alter in volume and weight—due to oxidation—on exposure to superheated steam to a much greater extent than the denser small-flaked irons. Since these effects may be accompanied by a serious falling-off in the strength, low silicon irons are to be preferred for such purposes.

Tensile tests at elevated temperatures indicate that cast iron retains its strength up to about 400° C., and the strength is rendered more permanent by the introduction of small amounts of chromium. Many cast-iron failures are attributable to the serious falling-off in properties accompanying growth, but it is also interesting to note that Hurst,‡ as the result of very considerable experience, considers that the cracking of many Diesel engine piston tops can also be attributed to a high phosphorus content in the iron, and regards 0·4 per cent P as the maximum limit.

Alloy Cast Irons.

Until comparatively recently, alloying elements were not, in general, intentionally added to cast iron, one notable exception, however, being the irons used for safety-vault construction, which contain high percentages of chromium and manganese. These elements tend to retain the carbon in the combined condition, and give a material which is intensely hard. If present in sufficient quantity, they have the same effect as increasing the carbon content beyond 4·3 per cent (p. 93).

The beneficial effects brought about by the introduction of nickel and chromium into cast iron are now becoming more generally recognized. *Nickel*, like silicon, promotes the decomposition of free carbide of iron, but the graphite plates so produced are very small. This feature, together with the hardening effect that nickel has on the iron (ferrite) itself, results in increased strength and hardness. According to Hanson,§ however, the nickel addition must be made at the expense of silicon in order to obtain the most beneficial results. Ordinarily, chill effects can be

* *Journ. Iron and Steel Inst.*, 1909 (ii), 1911 (i). † " Die Giesserei ", 1926.
‡ *J.I.S.I.*, 1917, No. II. § *Mond Nickel Bulletin*, Series B, No. 5.

completely eliminated by an increased silicon content; but, since this may cause the formation of large graphite plates and a very " open " grain, physical properties may result which are not desirable.   Hanson, however, considers that nickel additions up to 2·3 per cent actually refine the grain of ordinary engineering castings, although little refinement is effected in irons containing much silicon.   A substitution of two parts of nickel for one part of silicon is therefore suggested for most purposes.   As the result of experiments conducted under Hanson's supervision,* the following conclusions have been arrived at:

(1) Like silicon, nickel eliminates or reduces chill.

(2) Nickel assists in the formation of graphite, but the graphite is much finer than that obtained with silicon; and even in the presence of much silicon, small amounts of nickel tend to reduce the size of the graphite plates, and also to improve the machinability.

(3) Unlike silicon, nickel does not decompose the carbide of pearlite, but refines and hardens this constituent.

Full-scale experiments on high-grade automobile engine iron gave the following results:

	Total Carbon.	Si.	Mn.	S.	P.	Ni.	Cwt.	Transverse Tests.			
								Deflection.	Modulus of Rupture.	Tensile M.S. ·55" Section.	Brinell on Cylinder Wall.
Plain iron	3·27	2·05	·92	·110	·176	nil	26·7	·36"	35·4	14·2	180
Nickel iron	3·20	1·44	·91	·108	·170	1·12	28·4	·33"	37·6	20·5	215

The nickel iron showed a grey fracture for which the hardness figure was exceptionally high.

Chromium has also been introduced into ordinary cast iron, and is added either alone or with nickel.   Chromium resembles nickel in its power to strengthen the pearlite matrix, but differs from it in tending to inhibit graphite formation, and harden the iron by forming carbides of exceptional hardness.   Chromium therefore, accentuates any chilling effect, and is often intentionally introduced into irons for such purposes as chilled rolls, as little as 0·5 per cent apparently giving increased resistance to wear. In addition, this element reduces the expansion and contraction of castings subjected to repeated heatings.   Small amounts of chromium also bring about considerable grain refinement, which

is desirable in ordinary "grain" rolls used for roughing purposes, for sections and where the metal is finished hot; also for the moulds used in the casting of steel ingots.

A disadvantage of chromium is that it tends to yield irons containing hard carbide " spots " which hinder machining. This carbide formation may be restricted by increasing the silicon, although this tends to open the grain, and the necessary combination of strength and machinability is best obtained by the addition of both nickel and chromium. In these cases, larger proportions of nickel are added than if chromium were completely absent. Hanson and Everest * found that the addition of 1·7 per cent Ni with 0·4 per cent Cr to an iron containing 3·4 per cent C, 1·24 per cent Si, and 0·54 per cent P had a markedly beneficial effect. This iron was used for the manufacture of cast-iron dies, the nickel and chromium producing a considerable increase in the hardness, without, however, increasing the amount of chill; and the dies had a greatly increased life.

Nickel-chrome cast-iron cylinder liners are now being used, containing as much as 4 per cent of nickel and 1 per cent of chromium. For this purpose hardness combined with machinability is essential, and a Brinell number of over 200 is usually asked for. A good quality cylinder iron suitable for particularly heavy work has the following composition:

T.C.	C.C.	Si.	Mn.	S.	P.	Ni.	Cr.
3·05	0·85	1·85	0·61	·086	·272	4·02	1·25

Brinell number, 289

Copper, usually with chromium and nickel, is introduced into many cast irons to improve the corrosion-resisting properties. Irons used for pump parts and in chemical plant may contain up to 3 per cent Cu, 12 per cent Ni, and 7 to 8 per cent Cr.

An alloy cast iron containing 10 to 15 per cent nickel and 5 to 10 per cent manganese, known as *Nomag,* is used for electrical castings, motor end-rigs, switch covers, insulator supports, and resistance grids. The alloy is practically non-magnetic and has a low permeability and high electrical resistance; and it is claimed that its use results in a considerable saving in electrical power in view of the cutting down of both magnetic and eddy current losses. Nomag is readily machinable.

Malleable Cast Iron.

Pig-iron is easily remelted and may be cast into almost any desired shape or form, but the castings are too weak and brittle for many purposes. By using irons of suitable composition, however, and subjecting the castings to an annealing process, practically the whole of the carbon may be converted into graphite which is embedded in the iron matrix, the product then resembling wrought iron in its general properties. Malleablized cast irons thus produced are stronger and, as the term suggests, much more malleable and ductile than ordinary cast iron.

The irons used must give white fractures after casting, since the graphite in ordinary grey irons is in the form of long curved plates, which would persist and tend to embrittle the iron after the malleablizing process had been carried out. Ordinary white irons are too viscous to run easily, but the necessary fluidity is obtained by using irons containing a fair amount of phosphorus (up to 0·25 per cent), together with a considerably lower carbon content than that of ordinary foundry iron. A fairly high silicon content is almost inevitable in view of the very high sulphur content of most white irons; and it has been suggested that silicon is essential to success in the malleablizing process.* The graphitizing effect of the silicon in the casting is overcome by using irons containing fair quantities of sulphur and low manganese; although the latter element should always be present in such quantity as to eliminate any detrimental effects due to the sulphur. In the absence of sufficient manganese, the sulphur exists as sulphide of iron, which is a very weak brittle substance, and its presence in the iron seriously impairs the mechanical properties. In the presence of manganese, however, manganese sulphide is formed instead which is comparatively harmless. In order to reduce the silicon in the iron to the desired extent, remelting in an oxidizing furnace or refinery may be carried out.

The original process for making malleable cast iron, first described by Réaumur, consisted in packing the white iron castings in hematite iron ore and then heating them to a temperature between 800° C. and 900° C. for quite a long time. This method is still practised in this country and on the Continent of Europe. During heating, the interior carbon diffuses outwards and is oxidized at the surface, which results in a great reduction in the

* James, *J.I.S.I.*, 1900 (ii)

(a)   (b)

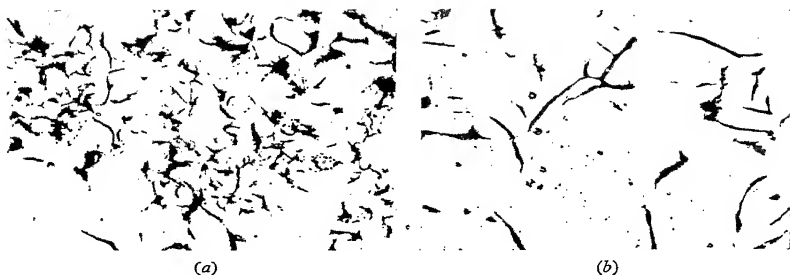Fig. 6.—Micrographs of two cast-iron bottle moulds.   Unetched.   × 200.
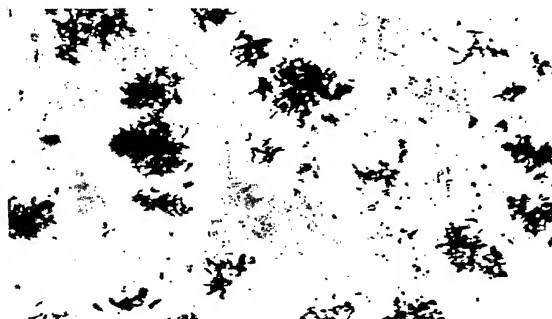(a) gave good results, whereas (b) proved unsatisfactory

Fig. 7.—English malleable cast iron.   × 100.   Graphite "rosettes"
with some pearlite in ferrite matrix
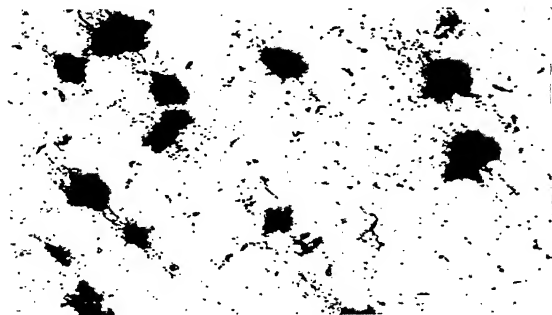
Fig. 8.—American "blackheart" casting—near centre.   × 100.
Graphite nodules (black) in ferrite background.   The small
particles are coalesced iron carbide.

total carbon content and the production of a heavily decarburized outer layer or " skin ". At the same time, both during heating and cooling, the iron carbide undergoes decomposition, but the graphite so formed exists as grains or " rosettes " embedded in the soft iron matrix. In this form the graphite does not seriously weaken the iron. Fig. 7 shows a section of a good quality English malleable cast iron. In extreme cases, the above treatment results in almost complete decarburization, the product then being known as *whiteheart* malleable cast iron. Such irons, when subjected to microscopic examination, often show the holes originally occupied by the graphite. This latter treatment is rather too drastic for certain purposes as there is always the possibility of the formation of intercrystalline oxide films in the skin, with the consequent risk of surface crack development.

American practice consists in heating the castings in a non-oxidizing atmosphere and generally at a much lower temperature (about 750° C.); graphitization then being obtained without any appreciable loss in carbon. The graphite gives a black velvety appearance to the fractures to which the term *blackheart* is applied. Fig. 8 is a photomicrograph of the section of a blackheart cast-iron part having the following composition:

Total carbon, 1·98; combined carbon, trace; Si, 1·2; S, 0·057; P, 0·172; Mn, 0·3.

This iron proved very satisfactory in service, the following mechanical test results being obtained:

Max. Stress, 25·72 tons per sq. in.
Elongation, 14 per cent.
Brinell No., 143–148.

Fig. 9 is from a casting of identical size and design with the above. This iron failed with disastrous results, which is not surprising in view of the following chemical analysis:

Total carbon, 2·6; combined carbon, 0·51; Si, 0·574; S, 0·167; P, 0·059; Mn, 0·15.

The sulphur content is obviously much too high, which, together with the low manganese, accounts for the very poor tests given.

Max. Stress, 22·24 tons per sq. in.
Elongation, 1 per cent
Brinell No., 166–170.

The total carbon content is also higher than is usual in such materials. The photograph shows distinct evidence of under-

annealing, and although some improvement in properties was obtained by heating the material for a further period of 4 hours at 700° C., and cooling very slowly, the ductility value was even then greatly inferior to that of the blackheart iron.

During the annealing of malleable iron castings, a certain amount of shrinkage is generally observed due to the volume occupied by the separated graphite. This effect, however, is less pronounced in blackheart irons.

The Conversion of Pig-iron into Wrought Iron

The impurities in pig-iron—carbon, silicon, sulphur, and phosphorus—enter the iron as the result of the reducing character of the conditions which prevail in the blast-furnace. Oxidizing conditions are therefore necessary to bring about their removal from the iron, which is purified in furnaces known as " fineries " or hearths.

In *Sweden* the purification is carried out chiefly by either the Walloon or the Swedish Lancashire hearth finery process. These are similar in principle, although in the Walloon process the operations are carried out at much lower temperatures. Oxidation of the impurities is effected by the admission of air, under pressure, through twyers; and charcoal is used as the fuel. White pigs containing little silicon are used, and these are made from ores of exceptional purity. After melting, and under the action of the blast, silicon and manganese are oxidized first, and afterwards the carbon; the melting-point rises from 1200° C. to a temperature above that of the furnace. Some of the iron is oxidized to ferrous oxide (FeO), which forms a " cinder " with the silica and manganous oxide. Globules of solid metal containing about 0·8 per cent of carbon are thus formed, and these are held together by the more impure liquid iron remaining. The whole mass is then gathered together into a " ball " containing large quantities of liquid cinder (slag). This ball, which is not homogeneous, is taken to a steam-hammer and there knocked into a " bloom ", whereby most of the slag is expressed and the metal rendered more compact. The bloom is next cut into parts, each part being reheated, and in the Walloon process rehammered into a bar 3 in. by $\frac{1}{2}$ in. in section. In the Lancashire process the bars are finished by rolling. By this time nearly all the carbon has been oxidized and the finished bar may contain as little as 0·02 per cent.

Fig. 9.—Malleable cast iron. × 100. Incompletely malleablized as evidenced by the pearlite matrix
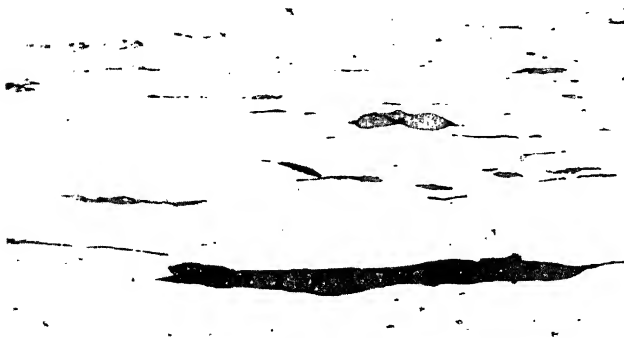
Fig. 10.—Longitudinal section of Swedish wrought iron. Unetched. × 100. Showing slag streaks. Note the composite nature of the slag

Fig. 11.—Showing the fibrous character of good wrought iron

Walloon irons constitute the basis for the finest tool and "shear" steels; and, although Lancashire irons are used for the same purposes, they are generally regarded as being inferior in quality. Ordinary chemical analyses show very little difference, the following being typical of either process:

C, 0·06; Si, 0·03; Mn, 0·1; S, 0·01; P, 0·013,

with the following tests:

| Yield-point, 12 tons per sq. in. | Elongation (on 2″), 40 per cent. |
| Max. stress, 21 tons per sq. in. | Reduction of area, 70 per cent. |

Micro-examination of wrought iron invariably reveals considerable quantities of involved slag. This is well shown in fig. 10, which is a longitudinal section, the slag being drawn out in the direction of rolling. The presence of these slag fibres distinguishes wrought iron from mild steel. Wrought iron has never really been melted, and when the material is melted, practically all the slag is got rid of, so that the product is mild steel.

The Puddling or Pig-boiling Process.

Swedish irons are comparatively low in silicon, and many of the white irons contain very little sulphur. On the contrary, the English white irons contain too much sulphur to be of real value for the production of wrought iron, and the only suitable irons are grey, which, however, are rich in silicon. Practically the only English process now carried on for the production of wrought iron is the puddling process, which depends on the reaction between the impurities in the molten pig and added oxides of iron. Either grey or mottled pig-irons may be used, but generally forge irons are employed. The lining of the furnace, together with the oxides added during the process, are known as "fettling". Fettling materials embrace various oxides:

(1) Hammer slag, which is essentially a silicate of iron, squeezed from the balls of iron, the chief function of which is to provide a bath of fluid material into which globules of iron trickle as they form.

(2) Cinder, which is tapped from the furnace and calcined, is used for the hearth itself.

(3) Red hematite ore, which is added during the process.

The bed of fettling rests on cast-iron plates, and the relining is done with a mixture of cinder and oxide. The bed is shaped and then covered with rolling mill scale, which softens under

heat. A ball of scrap iron is next charged, the temperature is raised, and the iron worked over the whole bed. The strongly oxidizing atmosphere maintained converts the iron into magnetic oxide (Fe_3O_4), which flows over the surface and gives a smooth even mass. A good bed is essential for the production of good quality iron. Pig to the extent of about $4\frac{1}{2}$ cwt. is then charged along with the necessary amount of millscale, and the process may be divided into four stages, viz.:

(a) Melting, which takes about half an hour. During this period some of the silicon, manganese, and phosphorus is removed.

(b) A 7 to 10 minutes' period, during which practically all the silicon and manganese is oxidized, along with a further amount of the phosphorus.

(c) The " boil ", lasting about half an hour, during which period the greater part of the carbon is oxidized, the gases formed bubbling through the liquid metal and burning with small blue flames. Further phosphorus oxidation occurs during this period.

(d) The final stage, occupying some 20 minutes. During this period, as the carbon is oxidized, the melting-point rises and the metal becomes pasty. The temperature is raised to a welding heat, and the iron is gathered together in the form of lumps of convenient size. These are taken to a hammer and knocked into blooms in order to expel as much slag as possible, after which the blooms are rolled into the " puddled " bars of commerce. The chemical changes which occur during puddling are indicated by the following figures, due to McNair:

	C.	Si.	Mn.	P.	S.
Composition of pig-iron	3·27	1·88	1·00	0·85	0·15
,, when melted	2·95	·41	·28	·58	—
Metal boiling	2·10	·18	·10	·21	—
12 minutes later	1·20	·20	·06	·14	—
" Balled " metal	0·61	·21	·05	·11	—
Finished product	0·18	·22	·05	·15	—

Nature and Uses of Wrought Iron.

Puddled iron is a suitable material for many purposes, particularly where ease in welding and working is desired. It withstands repeated heatings and forgings without deterioration, is tough, and may be bent almost double without any sign of fracture. Typical tests show a tensile strength of 22 to 24 tons per square inch, and 10 to 25 per cent elongation. The fibrous character of good wrought iron is well exemplified in fig. 11 (facing p. 22),

Fig. 12.—Fractured wrought-iron bolt. Unetched. × 100.
Showing massive and minute particles of slag

Fig. 13.—Cross-section of ingot showing blow-holes. Etched
with dilute nitric acid and reduced to ⅝ size. Note the small
crystal structure.

which is a photograph of a 2 in. square bar after bending through an angle of 180°. The iron did not fracture completely, but split along the slag fibres. This splitting before fracture is useful, since it serves as a warning when failure occurs, by which serious damage may, in some cases, be avoided. The fibrous nature of wrought iron is associated with the contained slag fibres, which are best observed when the unetched polished sections are examined under the microscope.

Too low a carbon content and large quantities of cinder may render the material weak and unsuitable for certain purposes. Fig. 12 is a section of a fractured wrought-iron bolt, the failure of which caused a great deal of inconvenience; and, in this case, a mild " free-cutting " steel would have been preferable. Within comparatively recent years, large quantities of so-called wrought iron have been made by welding together mild-steel bars containing considerable quantities of manganese, in the presence of slag, the product then being almost indistinguishable from the genuine welded puddled bars. The material is, however, by no means so satisfactory, and this has in all probability been responsible for the assumed deterioration in the quality of the genuine iron. Consequently, official specifications have been drafted whereby, if the material contains manganese in excess of 0·15 per cent, it is not regarded as wrought iron, and it is hoped that this will result in the wider use of the genuine puddled product, with a consequent revival of this old-established industry. Microscopically, puddled iron is very uneven in texture, and bands of almost pure iron may alternate with areas containing as much as 0·3 per cent of carbon. Puddled iron is used for general blacksmith's work, ornamental work, railings, links and couplings, horseshoes, &c.

Other Kinds of Iron.

Other commercial forms of the element are " Armco " iron and electrolytic iron. Armco iron is made in the basic open-hearth furnace, the carbon, silicon, manganese, sulphur, and phosphorus in the charge being oxidized by additions of iron ore until only traces of these remain. The metal really becomes over-oxidized, and the iron therefore contains fair quantities of iron oxide.

Electrolytic iron is chemically pure, excepting for occluded hydrogen. The latter embrittles the material, which is therefore unsuitable for any engineering purposes.

Steel—its Manufacture, Properties, and Uses

The Manufacture of Steel

Practically all the present-day steels are prepared from the product of the blast-furnace, i.e. they are not manufactured directly from the ore. Many attempts have been made to obtain iron and steel direct from the ore without the intermediate production of pig-iron. The later methods involve low temperature reduction by means of powdered charcoal. None of these direct processes has yet proved commercially sound, owing to the fact that the products are much too heterogeneous in nature, and, in most cases, are contaminated with the fuel used and with impurities contained in the ore.

Four chief methods are employed for the manufacture of steel: the crucible, Bessemer, Siemens, and electric-furnace processes. The crucible process is used chiefly for tool steel manufacture, whereas the lower carbon structural steels are the principal products of the Bessemer and Siemens processes. Steels of almost any description are made in the electric furnace, but generally tool steels are made in furnaces of small capacity, the larger electric furnaces being used mostly for alloy steels of the nickel and nickel-chrome types.

The only other process worthy of mention by which steel is produced is the cementation process. Swedish wrought-iron bars are packed in charcoal in air-tight fire-stone chests heated in special furnaces. The iron never becomes fluid, but as the temperature rises (to about 1100° C.), carbon begins to diffuse into the iron; an instance of diffusion in the solid state. At the same time, some of the diffused carbon reacts with oxide of iron in the contained slag, liberating carbon monoxide, which blows bubbles in the plastic steel, with the consequence that the bars, after cooling down, are covered with blisters, the product then being known as " blister " steel. The carbon content of the resulting bars under-

goes continuous variation from the outside to the centre, and the material is much too brittle to be of any practical use without further treatment.   The bars are therefore reheated and re-hammered so as to close up the blisters and render the mass more compact.   Several lengths of this " plated " bar are then welded together, rehammered, and then usually rolled down to the re-quired size.   During these reheatings, further diffusion of the carbon occurs, and the material becomes more homogeneous, although the weld-lines can always be observed in the final pro-duct, which is then known as " shear steel ".   Owing to the weld-lines, shear steel is always worked " on the flat ", and is never " up-ended ", otherwise there is always the risk of the develop-ment of cracks.   After subjection to further welding and rolling, the product is known as " double shear steel ", a material which is still unsurpassed for table cutlery, and other purposes, where an extremely keen cutting edge is desired.   Shear steel is the purest steel made, and is still produced, but, owing to its relatively high cost, to a limited extent only.

The Crucible Process.

In view of the fact that this was the first process in which steel was obtained in a perfectly fluid condition, the product became known as crucible " cast " steel.   The term is apt to be misleading, but " cast steels " are generally understood to be crucible furnace products.

The process consists essentially in melting specially chosen materials in fireclay crucibles or " pots " in order to obtain a product of the desired composition.   Fireclays are essentially hydrated silicates of alumina, the silica content being usually more than is required to combine with all the bases present, and so must be regarded as acid materials.   Since the removal of sulphur and phosphorus necessitates basic conditions, no refinement of the molten metal occurs, and in order to keep these two elements down to the specified low limits, the charges must necessarily contain small percentages only.   Many crucible steels are used for the manufacture of high-class cutting tools, which generally contain high percentages of carbon.   Sulphur and phosphorus exert a particularly harmful influence on the properties of such steels, and, in general, 0·035 per cent of either element is regarded as a maxi-mum.   The fuel used in the furnace is high-grade coke, which, however, always contains a considerable quantity of sulphur; and

the sulphurous gases generated during combustion permeate the pot walls and increase the sulphur content of the contained metal, although this increase seldom exceeds 0·02 per cent if the sulphur in the coke is less than 1 per cent. No alteration in the phosphorus content occurs, except perhaps a very slight increase due to concentration, when very dirty materials are charged. Silicon also lowers the quality of cutting steels, and the first consideration, therefore, for materials suitable for the manufacture of crucible steel is comparative freedom from silicon, sulphur, and phosphorus, conditions which are only rigidly satisfied by materials of Swedish origin made from pure magnetic iron ores. The materials exported from Sweden for this purpose are white pig-iron and wrought-iron bars. As already mentioned, Swedish bar iron is converted into blister steel by carburization in the cementation furnace; and these Swedish " cemented " or " converted " bar steels, together with either of the above two raw materials, constitute the charges for the production of the finest quality crucible cast steels. Numerous brands of bar iron are on the market, made chiefly by the Walloon and Swedish Lancashire hearth processes, the latter being the cheaper. The steels produced from Walloon irons are, in general, superior in quality, and the reason appears to lie in the greater freedom from dissolved iron oxide. Although Walloon irons are much more expensive, many high-class steel-makers willingly pay the increased price rather than risk the production of inferior quality steels. Scrap materials from crucible steels often constitute part of the charge, although the constant remelting of scrap may result in a considerable increase in the sulphur content. Swedish Bessemer scrap has also found great favour amongst steel-makers, and excellent results are obtained by its use. American washed metal—a refined pig-iron—is sometimes substituted for Swedish white iron, and when melted along with acid Siemens boiler-plate scrap, yields a product containing low silicon, sulphur, and phosphorus; but such mixtures should not be regarded as high-quality materials. Charcoal is often used as a cheap carburizing agent.

The Bessemer Process.

This process consists essentially in oxidizing the impurities in molten pig-iron by blowing air through it. The vessel in which this is carried out is known as a converter, and consists of a mild-steel shell lined with some refractory material, either acid or

basic in character, according to the composition of the pig-iron available. The pig-iron, usually of mixed brands, is melted in a cupola together with steel scrap, coke, limestone, and a little fluorspar; the molten metal is then transferred to the converter for conversion into steel. The Stock converter is unique in the respect that melting and blowing are carried out in the same vessel. Oil fuel is used for melting in the Stock furnace, and the air necessary for combustion is preheated by the hot products of combustion.

In the ordinary Bessemer process, no further external supply of heat is available after the metal is in the converter, and the heat necessary to maintain the metal in a molten condition throughout the process is generated by the oxidation of the impurities contained in the charge. The elements carbon, silicon, manganese, and phosphorus therefore act as internal fuels.

With large Bessemer plants, in order to obtain greater regularity in composition, the use of the hot metal " mixer " has proved invaluable. Mixers are huge receptacles for the storage of molten pig-iron and are either acid or basic-lined, according to the type of pig-iron produced in the blast-furnace. They are usually gas-fired on the same principle as the Siemens furnace. The molten pig-iron is transferred from the blast-furnace to the mixer, and from this the amount required for the Bessemer converter is drawn at intervals. Some oxidation of manganese and silicon occurs in the mixer, and, in basic-lined vessels, an appreciable quantity of sulphur is also removed.

Various modifications of the original Bessemer converter are in use, depending chiefly on the method of blowing. In the ordinary pear-shaped vessel, the blast enters through fireclay twyers in the bottom of the lining, but surface and side-blowing methods, such as that adopted in the Tropenas converter, have been extensively employed. The method of producing steel, however, is practically the same in most of the processes, and consists in oxidizing the impurities in the charge by the oxygen of the air blown in, so as to produce almost pure iron, which is then recarburized to the desired extent.

Refractory Materials

The materials used for the linings of metallurgical furnaces are naturally occurring substances which are generally subjected

to some preliminary calcining treatment, although in certain cases they are used in a more or less raw state. These materials must be sufficiently refractory in nature to withstand high temperatures without fusing, when in contact with molten metal, for which they must provide a safe receptacle. In addition, they must resist erosion to a marked extent by molten slag, and must also be capable of withstanding a certain amount of pressure. Refractory materials for this purpose may be divided into three classes according to their chemical behaviour at high temperatures.

Acid refractories usually contain considerable quantities of silica. Sand, ganister, and some fireclays are important members of this class. Sands which are used for furnace work usually contain more than 97 per cent of silica (SiO_2). Such sands are really too refractory in nature if used alone, and are therefore generally mixed with a small proportion of red sand. The latter contains a certain proportion of oxide of iron, which forms a more readily fusible silicate, and this acts as a bond by cementing the grains of silica together. Ganister is a siliceous rock, the impurities in which act as a cementing material between the quartz (silica) crystals. The material is thus self-bonding, and after being ground and moistened with water, may be rammed into position. On heating, ganister sets very hard indeed, and is one of the most useful refractories. It is used for the linings of the acid Bessemer and electric furnaces, and also for the manufacture of silica bricks. The roofs and walls of almost all the larger steel-making furnaces are built up with silica bricks.

Basic Refractories.—In this class silica is either altogether absent, or is present in such small quantities that basic oxides predominate. Examples of this class are dolomite, magnesite, and lime (calcined limestone). Raw dolomite is essentially a mixture of the carbonates of lime and magnesia, the two oxides being isomorphous. The material must be calcined and " dead-burnt " before use. The calcination, which removes carbon dioxide, is complete after heating to 900° C. for a few hours. Magnesite consists essentially of magnesium carbonate, and is dead-burnt before use, just as in the case of dolomite, although the temperature of calcination is much higher. Dolomite is used for the linings of basic Bessemer, Siemens, and electric furnaces. This use permits of the production of slags which are also very basic in character. Such slags are essential for the removal of sulphur and phosphorus from molten iron and steel. Unfortunately, cal-

cined dolomite " perishes " and disintegrates on standing, owing to the action of atmospheric moisture and carbon dioxide, and can only be used, therefore, in furnaces which are being worked continuously. This difficulty does not arise with magnesite, which is the only suitable basic material for the linings of furnaces which are worked intermittently. Both materials are generally mixed with hot anhydrous tar, and are either rammed into position or put in, under heat, layer by layer. Magnesite is much more expensive than dolomite, and this restricts the wider use of the material. Magnesite is also used for the manufacture of bricks for the foundations and walls of many basic furnaces. Lime is not used for linings, but is the chief constituent of basic slags.

Neutral Refractories.—In this case the acid and basic constituents are evenly balanced, or else the substance itself is of chemically neutral behaviour. Chrome bricks, graphite, carborundum, and some fireclays are examples of this class. Chrome bricks are made from natural chromite or chrome iron ore, and are often used to separate the silica and magnesite bricks, of which the walls of most basic furnaces are made. Chemical action also takes place between fireclay and magnesia at high temperatures if the two materials are not separated by a layer of chrome bricks

The Acid Bessemer Process

The lining of the furnace is rammed ganister, and consequently no removal of sulphur or phosphorus occurs. Silicon is essential as a fuel, and the pig-irons employed are manufactured from the purest hematite iron ores. Compositions of these irons have been given on p. 8. The average silicon content of the iron charged into the cupola is generally about 2 per cent, which may be decreased during melting to about 1·8 per cent. A slight increase in the sulphur always occurs, and the composition of the liquid metal which is then run into the converter is as follows:

C, 3·0; Si, 1·5–2; Mn, 0·5–1; S, less than 0·06; P, less than 0·06.

As silicon is the internal fuel, sufficient must be present to obtain and maintain the necessary high temperature, and any deficiency of the element is made up by the addition of ferro-silicon before the blow is commenced. The temperature of the cupola or mixer metal is also of great importance, since if the metal is very hot, oxidation of the carbon may occur in preference to that of the

silicon, and if the silicon is not removed in the early stages of the blow, high silicon steels are produced. High temperatures are corrected very effectively by the addition of cold steel scrap.

The acid blow may be divided into three stages:

(*a*) When the silicon is being rapidly oxidized to silica, which floats as a scum or slag on the surface of the metal.

(*b*) When the silicon content of the melt is sufficiently reduced, oxidation of the carbon begins, with the liberation of carbon monoxide, which bubbles through the heavy slag and burns with an appreciable flame at the converter " mouth ". This stage is known as the " boil ", and during this period particles of white-hot slag and metal are ejected into the atmosphere.

(*c*) When the carbon has been almost completely oxidized, the final stage is reached, the end of the blow being taken when the flame suddenly drops. Great experience is necessary at this point, since if the metal is " over-blown " for only 15 seconds, steels containing a large proportion of iron oxide are obtained; the losses of the finishing alloys are excessive, and poor steels, low in manganese, are produced. On the other hand, " under-blowing " will yield steels with higher carbon, silicon, and manganese contents than is desirable. The duration of a blow obviously depends on the amounts of these three elements in the cupola metal, but with an initial silicon content of about 2 per cent, the time taken is about 20 minutes. The composition of the blown metal varies between the following limits:

C, 0·04–0·08; Si, 0·02–0·07; Mn traces, 0·08; S, 0·04; P, 0·04.

Deoxidation and recarburization are then brought about by additions of alloys containing manganese, which are thrown into the converter with considerable force so as to penetrate the heavy slag. The manganese may be added in either of two forms: an iron-manganese alloy containing from 12 to 20 per cent of manganese, known as spiegel, and ferro-manganese containing about 80 per cent of the element. Some of the added manganese reacts with oxide of iron in the steel according to the reaction:

$$FeO + Mn = MnO + Fe.$$

The manganous oxide thus formed, unlike ferrous oxide, is insoluble in the molten steel and rises to the surface. Spiegel contains between 2 and 4 per cent of carbon, and ferro-manganese about 6 to 7 per cent. Both materials are therefore carburizing

alloys.   If much recarburization is necessary, molten pig-iron from the cupola or mixer may be used, provided that the silicon content is not increased beyond specification limits.   The method is quite suitable for steel castings, where a silicon content greater than that of most steel ingots is permissible.

The metal contains more oxide of iron than that made by any other process, and sufficient manganese is usually added to reduce this effectively and leave about 1 per cent of this element in the finished steel.   Steels for castings may contain 0·2 to 0·6 per cent silicon, and about 0·8 per cent manganese.   A small quantity of aluminium is also added.   The loss in weight of the charge due to oxidation of the iron and impurities varies between 12 and 16 per cent, and this concentration results in slightly increased sulphur and phosphorus.

The Steels produced by the Acid Bessemer Process.

Although steels produced by the acid Bessemer process are not generally regarded as being equal in quality to acid Siemens steels, they are frequently used for similar purposes with quite satisfactory results.   Alloy steels have been made to an appreciable extent by this process, whilst steel castings are made in large quantities, particularly in Tropenas plants, the high temperatures obtainable yielding very fluid metal suitable for castings.   Some specifications for acid steel castings are given in the following table·

C.	Si.	Mn.	S.	P.	Cr.	Purposes for which used.
0·4–0·45	0·3–0·4	0·75–0·85	0·06	0·07		Ordinary castings.
0·7–0·8	0·4–0·5	0·75–0·85	0·05	0·06	0·5–1·0	Castings for wearing and crushing.
0·2–0·25	0·2–0·25	0·5–0·6	0·03	0·04		Castings for wheel centres.
0·3–0·35	0·5–0·6	0·8–0·9	0·05	0·06		Machinable castings.
1·0–1·25	0·2–0·3	10·0–12·0	0·05	0·06		Manganese steel.
0·4–0·6	0·4–0·6	0·8–0·9	0·05	0·06		Castings under pressure.
0·1–0·2	0·1–0·3	0·2–0·4	0·05	0·06		Electrical castings.

American and Swedish Bessemer Practice.

In America, charges containing lower silicon—1 per cent—are employed, and in order to obtain the necessary high temperatures these charges must follow each other very quickly.   On this account it is to be feared that insufficient time is allowed for deoxidation, and American Bessemer steels are usually regarded as being inferior to those produced by the English process.

In Sweden, pig-irons containing about 1 per cent of silicon and from 2 to 4 per cent of manganese are employed, and the blow is ceased when the carbon is down to the required value. Since the metal always contains a considerable amount of manganese, the bath is never greatly impregnated with dissolved oxides; consequently no manganese additions for deoxidation are necessary. A residual manganese content of 0·3 to 0·5 per cent is generally obtained, and the steels are of excellent quality. Swedish Bessemer steels are rightly regarded as high-class material, and for certain purposes are almost as good as crucible steel. The following composition is typical of Swedish Bessemer spring steel:

C, 0·65; Si, 0·06; Mn, 0·32; S, 0·02; P, 0·025.

The Basic Bessemer Process.

The basic process, originally invented in 1879 by Thomas and Gilchrist, is not used in this country to any extent nowadays, but enormous quantities of basic Bessemer steel are produced on the Continent. This is due to the fact that the English low-grade ores are too siliceous in character, the pig-irons produced from them containing either too much silicon or too little manganese, and it is necessary to use a certain proportion of imported manganiferous ore as part of the blast-furnace charge in order to obtain the necessary composition for the fluid metal. On the other hand, the native ores of Germany, France, and Austria, although highly phosphoric, yield pig-irons which are most suitable for the basic Bessemer process.

The lining of the vessel consists essentially of rammed dolomite, and high phosphorus charges can be almost completely dephosphorized. A high phosphorus charge is indeed almost a necessity, in order to enrich the slag with phosphates and make it of commercial value as an artificial manure. Silicon is essential in the acid process in order to generate the heat required during the blow. Too much silicon in a basic charge, however, yields an acid siliceous slag which may attack and seriously damage the basic material with which the converter is lined. Silica also retards dephosphorization, and it is therefore necessary to use some other element as the chief internal fuel. The most suitable irons are those containing considerable amounts of manganese, with as low a silicon content as possible. The manganese generates heat during its oxidation to manganous oxide, which is basic in character and

thus counteracts acidity due to oxidized silicon. Manganese prevents over-oxidation of the metal, and also tends to eliminate sulphur, although to a limited extent only. The oxidation of phosphorus is extremely exothermic, and this supplies the heat in the later stages of the process.

The pig-iron may be transferred to the converter directly from the blast-furnace, but is often remelted in the cupola; and just as with the acid process, in large basic plants metal mixers are utilized with much benefit. The sulphur content of the iron is lowered in the basic-lined mixer if the manganese content is sufficiently high, and some silicon is also oxidized. The basic process consists in charging the molten pig-iron into the hot converter, lime being charged either before or whilst the metal is running into the vessel in order to neutralize all the silica that may be formed. A slag rich in lime is thus produced. If excess lime is not added, a siliceous slag is formed which attacks and may seriously damage the dolomite lining of the furnace. Silicon, carbon, and manganese are oxidized first, but only a small amount of phosphorus is removed in the earlier stages. When the carbon has been almost completely oxidized and the flame drops, the blow is not discontinued as in the acid process, but is carried still further in order to oxidize and remove the phosphorus from the metal to the slag. This last stage is known as the " after-blow ", and great experience is necessary to produce good steel. Over-blowing results in the production of over-oxidized and " wild " metal, whilst if under-blown, the steels are rich in phosphorus. Temperature plays an important rôle in basic Bessemer practice. A high temperature is preferable during the blow proper, so as to oxidize practically the whole of the silicon and carbon and leave most of the manganese and phosphorus unoxidized. With a comparatively low temperature, the phosphorus, manganese, and some iron are oxidized first, and the after-blow then badly over-oxidizes the metal. A comparatively low temperature is desirable during the after-blow, in order to remove the phosphorus but to avoid complete oxidation of the residual manganese, which, with good practice, is generally not less than 0·15 to 0·2 per cent at the end of the process. Over-oxidation of the metal is thus avoided, and the steels produced are sometimes of better quality than those made in the acid converter. The temperature is somewhat controlled by adding only part of the total lime until the carbon has been removed. The remaining lime is then added, which cools

the metal, just before the commencement of the after-blow. The following data give some idea of the chemical changes which occur:

Blowing Time.		C.	Si.	Mn.	S.	P.
Pig-iron,	0 min.	3·354	0·481	0·85	0·177	2·009
	6 ,,	1·321	0·009	0·45	0·128	1·786
	9 ,,	0·094	0·005	0·52	0·112	1·436
	12 ,,	0·015	0·009	0·34	0·084	0·117
	15 ,,	0·016	0·013	0·23	0·077	0·066
Finished steel		0·26	0·033	0·88	0·059	0·097

Additions of silicon and manganese at the end of the process are made by means of ferro-silicon and alloys of iron and manganese. The last-named introduce the requisite amounts of both carbon and manganese. Molten basic pig-iron, in view of its high phosphorus content, is obviously out of the question as a recarburizer.

Uses of Basic Bessemer Steel.

Steels for the manufacture of rails, tyres, axles, boiler and ship plates, girders, and all kinds of bridge and structural sections, wire, bolts, and forgings of almost any description, are regularly made by the basic Bessemer process, and also large quantities of steel for castings.

The Siemens-Martin Open-hearth Process

In this process, pig-iron and steel scrap are melted in comparatively shallow hearths by means of the combustion of gas generated in producers near to the furnaces. Before entering the furnace chamber in which combustion occurs, the gas and the air necessary for combustion pass independently through one of two pairs of " regenerative " chambers containing firebricks arranged in " checker " fashion. The hot waste products of combustion, on their way to the chimney-stack, then pass through and give up a large quantity of heat to the other pair of regenerators. The direction of the gas, air, and waste gases is reversed every 20 to 30 minutes; and by this means the ingoing gas and air are raised to a temperature of about 900° C. before entering the hearth where combustion occurs. The additional heat of this produces the necessary high temperature. In order to ensure thorough mixing of the gas and air, the air enters the furnace chamber at a higher level than the gas.

As in the Bessemer process, the nature of the lining depends entirely on the kind of pig-iron which is charged, and the furnaces are either acid or basic-lined as the case may be.

The Acid Siemens Process.

The acid hearth consists essentially of silica in the form of " fritted " sand which is put in under heat, layer by layer. Owing to the acid character of the lining, charges must be low in sulphur and phosphorus. Further, no material low in silicon may be charged on to the banks or bed of an acid hearth, otherwise any oxide of iron produced by flame oxidation reacts with silica of the lining. By charging materials rich in silicon, silica is produced, which combines with any oxidized iron to yield a slag covering for the molten metal, and thus minimizes the erosive action on the lining. The oxidation of the silicon also generates heat, which assists in the melting of the charge.

The acid process consists in removing the manganese and silicon from the molten metal during the earlier stages, and then bringing down the carbon to the point desired by judicious additions or " feeds " of iron ore. Carbon monoxide is liberated, and bubbles through the slag so that the bath appears to boil.

Charges containing considerable proportions of carbon and silicon are therefore essential, and the only materials fulfilling the necessary conditions are the acid Bessemer and acid open-hearth pig-irons. These irons are melted together with some steel scrap, the relative proportions depending to a great extent on the class of steel required. High carbon steel " heats " require a larger proportion of pig-iron in order to give sufficient latitude for the " boiling-down ", but high pig-iron charges tend to prolong the process if mild carbon steels are to be produced. A high average silicon content also prolongs the period between the melted condition and the attainment of the boil, and an average silicon content of about 1 per cent is generally aimed at. This is enough to prevent over-oxidation of the metal during melting, although a " boil " is obtained shortly afterwards. The pig-iron is charged first, and the scrap on top of the pig. Some small increase in the sulphur content occurs during melting, due to that contained in the coal used in the gas-producers; the increase being more pronounced when light bulky scrap is used. Phosphorus may also increase due to bath concentration, and an allowance for a 0·01

per cent increase is usual. Manganese usually needs little consideration, and up to 1 per cent it is regarded as beneficial. Old broken ingot moulds are sometimes charged, but ought not to be used for the best quality steels.

When melted, the composition of the bath is determined by the rapid analysis of spoon samples, if these can be obtained. Iron ore is then added, and when the bath comes " on the boil ", spoon samples are taken every 10 or 15 minutes and their carbon contents determined. The carbon is almost constant near the end of the process, and in any event the rate of oxidation is such that the percentage of carbon falls not more than 0·2 per cent in the hour. In some cases ferro-silicon or silico-spiegel may be necessary to take the bath " off the boil ", in order to arrest the oxidation of the carbon. Silico-spiegel is a low-grade ferro-manganese containing 10 to 15 per cent silicon and up to 20 per cent manganese. It is essential that the full effect of the last ore addition be worked off near the end of the process, otherwise there is the possibility of a " wild " cast, with the production of steel ingots full of blow-holes. The hematite ore added during the process consists chiefly of ferric oxide (Fe_2O_3), but this is unstable at furnace temperatures, and dissociates into magnetic oxide (Fe_3O_4) and oxygen. This oxide then reacts with the carbon in the metal according to the reaction·

$$Fe_3O_4 + C = 3FeO + CO.$$
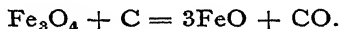
The liberated carbon monoxide dissolves in both slag and metal, and no appearance of boiling occurs until both solvents are saturated with the gas. Some of the ferrous oxide (FeO) combines directly with silica in the slag to form a silicate of iron; the remainder then dissolves in the slag, and, to a limited extent, in the metal also. Until this limit is reached, the concentration of the dissolved ferrous oxide in the metal is dependent on that in the slag. This is a point of great practical importance, and many steel-makers will not tap an acid open-hearth heat if the FeO content of the slag is greater than 17 per cent. Most of the oxide then exists in combination with silica and not in solution in the slag.

The oxidation of the carbon during the boil is due to the reaction between the dissolved ferrous oxide and the carbon in the metal, thus:

$$FeO + C = Fe + CO.$$
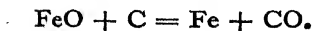
This decreases the oxide concentration in the metal, which is therefore accompanied by a decrease of the same in the slag, and thus involves a migration of FeO from slag to metal. Eventually a condition of equilibrium is obtained, owing to the reversibility of the above reaction, and hence no further oxidation of the carbon occurs. Additions of ore, however, disturb the equilibrium and promote further oxidation. When the carbon is down to the required value, equilibrium conditions are practically obtained, and the law of mass action can therefore be applied to the above reaction. Since the iron is acting as the solvent for the other reacting substances, its active mass may be regarded as constant, and the equilibrium conditions are then represented as follows:

$$\frac{\text{Concentration of CO}}{\text{Conc}^n \text{ of FeO} \times \text{Conc}^n \text{ of C}} = k.$$

k is therefore an equilibrium constant whose value depends solely on the temperature at which the reaction occurs. It is evident that for a given CO concentration the lower the carbon in the steel the greater will be the ferrous oxide concentration, and vice versa. This accounts for the greater difficulty, so well known to the practical steel-maker, in bringing about the thorough deoxidation of very low carbon steels, and hence the necessity for a higher manganese content in such steels. Very low carbon steels exhibit a greater tendency to rise in the moulds, particularly when cast at high temperatures. As a consequence also, the oxidation losses of the finishing elements are much greater the lower the carbon content of the bath. Deoxidation is carried out generally by the addition of spiegel to the bath, and of ferro-manganese in the ladle. About 30 per cent Mn is lost by oxidation when the materials are added in the furnace during the production of medium carbon steels, although the loss may be as high as 50 per cent in the case of low carbon steels.

The composition and constitution of the slag has a marked influence on the quality of the steels produced. Many high-class steels are finished with rather thicker slags containing an excess of silica. Under such circumstances reduction of some of the silica occurs, and the residual silicon content of the bath is therefore influenced by the acidity of slag, as is illustrated by the following typical figures:

SiO_2 in slag	..	..	51·00%	54·00%	57·00%
Si in steel	..	..	0·06	0·10	0·20

Under ordinary circumstances, the silica in the slag is about 50 per cent, giving a residual silicon of about 0·05 per cent in the steel. The silicon liberated from acid slags acts as a powerful deoxidant, and the steels are much better in consequence. The fact that many engineering specifications demand a maximum silicon content lower than 0·1 per cent is therefore to be deplored, since the element is a very valuable one for the production of sound steel.

Silicon may be present in structural steels to a much greater extent than in tool steels, and some open-hearth steels frequently contain as much as 0·25 per cent of the element.

In order to render the deoxidation as perfect as possible, small quantities of vanadium and titanium are sometimes added, certain railways asking for about 0·1 per cent Ti in the finished steel.

The Steels produced in Acid Open-hearth Furnaces.

The various classes of steel made in acid-lined furnaces are almost too numerous to mention. The carbon contents vary between 0·08 and 1·3 per cent, and alloy steels, particularly those containing nickel, with or without chromium, are made in large quantities. Some typical specifications for acid steels are given in the following table:

C.	Si.	Mn.	S.	P.	Ti.	Purposes for which used.
35–·50	·10	·7–1·0	·080	·075		Railway rails.
12–·25	—	·3–·5	·040	·040		Boiler fire-boxes.
25–·32	·20	1·0	·035	·035		Loco. crank axles.
·70	1·12	·33	—	—		Springs.
60–·70	·25	·7	·050	·050		Railway tyres.
55–·80	·12	·8	·035	·035		Laminated springs.
27–·35	·15	·6–·8	·050	·050		Piston-rods.
·25	·35	·8	·040	·050		Steel castings.
1·00	—	11·0–14·0	—	·100		Railway rails and tramway points and crossings.
75–·90	—	—	—	—	0·1	Railway rails.
30–·50	·10	·5–·8	·030	·030		Gun forgings.
10–·20	·10	·8	·040	·035		Case-hardening steel.

The Basic Siemens Process.

The hearth of the basic furnace consists of burnt dolomite. This is generally put in under heat, each successive layer being then saturated with basic slag. Owing to the basic nature of the lining and slag, dephosphorization is readily accomplished, and sulphur is also eliminated, but to a much lesser extent. Slags rich in phosphates are valuable by-products and are used as fertilizers.

The agricultural value of a slag is determined by the solubility of its contained phosphate in citric acid solutions. Fluorspar is employed in basic practice to yield fluid and workable slags, but, unfortunately, fluorspar decreases the phosphate solubility in citric acid and hence diminishes the value of the slag. An average charge of metal contains about 0·5 per cent phosphorus, and the sulphur content is kept below 0·15 per cent. The manganese in the charge is important since (1) by its oxidation to manganous oxide it supplies a base to combine with the silica; (2) it prevents over-oxidation of the molten metal, and (3) combines with sulphur to form manganese sulphide which is assumed to react with oxygen, liberating sulphur dioxide. Manganese is therefore an effective desulphurizing agent, and up to 1·5 per cent may be charged with benefit. Fluorspar is also supposed to remove sulphur directly, but there is little evidence in support of any direct action, although this material lowers the melting-point of high lime slags, which would otherwise be much too viscous for successful working.

A basic charge usually consists of grey phosphoric pig-iron, English white pig-iron (which contains too much sulphur for any other processes), and steel scrap. The carbon content of the finished steel largely determines that of the melt, the figure lying between 0·5 and 1·5 per cent. Average charges contain about equal proportions of pig-iron and scrap. The scrap is charged first, then lime or limestone, and the white and grey pig last of all. By this means, oxidized silicon from the pig-iron does not damage the furnace lining.

When the charge is completely fluid, the slag is rather viscous, and is then thinned sufficiently by the addition of fluorspar. Additions of millscale or iron ore, together with limestone, are made from time to time as the heat progresses. Millscale (Fe_3O_4) is generally preferred as the oxidizing medium, since the iron ore may contain much silica, and sufficient lime must be present throughout the heat so that there is an excess beyond that required to combine with all the silica and the oxidized phosphorus. Otherwise dephosphorization is retarded. In practice, carbon and phosphorus are oxidized together, ideal conditions being obtained when the dephosphorization is practically complete and the carbon is down to the desired value. Generally, however, it is necessary to continue the oxidation after the required carbon value has been reached in order to obtain a sufficiently low phosphorus content. The metal is then recarburized by the

addition of spiegel or low silicon pig-iron to the bath, or, more generally, by means of anthracite coal added in the ladle. Recarburization in the ladle is not altogether satisfactory, as there is the possibility that the molten metal may not be perfectly homogeneous.

Under good working conditions, a residual manganese content of 0·2 to 0·3 per cent is obtained in the steel, which is an insurance against excessive oxidation. The finishing slags, however, contain considerable amounts of ferrous oxide (up to 14 per cent), and this, unlike most of that in acid slags, exists in solution in the fluid slag and not in chemical combination with silica. The high ferrous oxide concentration in the slag most probably results in a higher oxide concentration in the steel than is met with in good acid practice, some indication of which is given by the fact that the oxidation losses of the finishing elements are generally greater than those which occur in the acid process.

The Steels made in the Basic Siemens Furnace.

The basic process is not so easily controlled as the acid process, and basic steels are generally regarded as inferior in quality, although no marked difference in chemical composition may be found. Properly made, however, and if the carbon is " caught " at the desired value, and particularly when manganese is present in the metal throughout the heat, basic steels give very satisfactory results for many purposes. Steels for girders, wire-ropes, tin-plates, and general structural purposes are made in enormous quantities, although comparatively little alloy steel has been made by this process.

Swedish Open-hearth Furnace Practice.

In Sweden the furnaces are of relatively small capacity and are mostly acid-lined. High pig-iron charges containing much manganese are employed, and the gas required for melting is generated from wood. The steels produced are extremely low in sulphur and phosphorus, and are of superior quality. Such steels as those used for tools and high-class ball-bearings are made, and give excellent results in practice.

The Manufacture of Steel in the Electric Furnace

In this country, most of the electric furnaces for steel production are of the " arc " type, the Héroult and Greaves-Etchells

furnaces predominating. The steel-making process is practically the same in any type of arc furnace, and, owing to the high price of electrical energy, it is necessary to be able to produce high quality steels from comparatively cheap scrap materials containing appreciable amounts of both sulphur and phosphorus. As a consequence, most furnaces operate with basic linings.

Basic Electric Furnace Practice.

Linings consist essentially of dolomite or magnesite, or of mixtures of these materials in varying proportions. Boiling anhydrous tar is employed as a bond whilst the lining is being rammed into position. Crushed basic slag is also mixed with the dolomite, and the silicates in it effectively cement the dolomite grains together at working temperatures.

Sulphur and phosphorus can be reduced to little more than traces if desired, but since no especial benefit is derived thereby, most specifications do not demand less than 0·015 per cent of either element. These elements can be removed from the molten metal in reasonable time if not exceeding 0·1 per cent originally, but if this value is exceeded the process is prolonged, and the current and electrode consumption and manufacturing costs increase. Scrap materials from acid and basic open-hearth or electric steels constitute almost entirely the basic electric furnace charge, and the process may be conveniently divided into three distinct stages.

The first stage consists in melting the scrap under oxidizing conditions in the presence of a highly basic slag, for the oxidation and removal of silicon and phosphorus. This slag is then removed by tilting the furnace, and the bath is recarburized, which constitutes the second stage. Finally, reducing conditions are obtained in order to bring about reduction of metallic oxides and removal of the sulphur.

The Melting-down Period.

As soon as a pool of molten metal forms between the electrodes, the slag-making materials—lime, iron ore, fluorspar, and sand—are added. Melting and oxidation then proceed simultaneously. Phosphorus is only completely oxidized when the carbon does not exceed 0·1 per cent, but a bath containing less than 0·05 per cent is almost certain to be over-oxidized and give trouble in the later stages of the process. Between these limits, dephosphorization

shortly after melting is almost assured without excessive bath oxidation. Spoon samples are extracted when the charge is completely molten, and these, when analysed, generally contain only small proportions of carbon, silicon, and phosphorus. Manganese is not so important, but below 0·05 per cent indicates some degree of over-oxidation. The first slag must be removed, since phosphates are reduced in the later stages of the process and the liberated phosphorus re-enters the metal. Slagging is a most important operation which has not always received the attention it deserves. Incomplete removal of the slag not only yields high phosphorus steels, but the greatest difficulty is experienced in thoroughly deoxidizing the metal. On the other hand, considerable quantities of steel may be removed with the slag, and the weight of the bath then becomes such a doubtful quantity that steels of indefinite composition are produced.

After the slag has been removed, the bath is carburized by means of anthracite coal, the metal being stirred with long wooden poles or " saplings ".

The next stage of the process consists in the deoxidation and desulphurization of the metal. For these purposes reducing conditions are essential, and are brought about by additions of lime, fluorspar, crushed coal or coke, and high-grade ferro-silicon. Coal and ferro-silicon reduce metallic oxides, and are direct desulphurizing agents, but no appreciable removal of sulphur occurs until the oxides of manganese and iron in the slag have been almost completely reduced. This reduction is indicated by a change in the appearance and colour of the slag, which goes from a more or less dense black or brown to an " open " or spongy almost perfect white. Under ideal conditions the slag undergoes a remarkable transformation on cooling, spontaneous disruption occurring after extraction from the furnace with the ultimate formation of an extremely fine white powder. The slag is then said to be " falling ", and a " white falling slag " is one of the best practical indications of good bath condition. The self-disintegration of basic electric furnace slags is in all probability due to the formation of Åkermanite $(2CaO \cdot MgO \cdot SiO_2)$ solid solutions, which, after solidification, suffer an enormous change in density at somewhat lower but definite temperatures. Calcium carbide is also formed, as is evident from the smell of acetylene when a slag is quenched in water.

Additions of ferro-silicon for deoxidation should be carefully

controlled, otherwise high silicon steels are produced. The average furnaceman is apt to regard ferro-silicon as an antidote for any poor bath condition. The condition of the slag is to be regarded as all-important. Equilibrium will be established between slag and metal if sufficient time is allowed, and with a good slag good sound metal samples are easily obtained. The sulphur existing in the steel as ferrous and manganese sulphides is removed by converting it into calcium sulphide, which is soluble in the slag but insoluble in the metal.

Far too much stress has been laid in the past on desulphurization and not enough on degasification. When carbon is used in the early stages of the deoxidation period, the heat should be finished with ferro-silicon, as the bath may contain dissolved carbon monoxide as a result of the reaction:

$$CaO + C + FeS = CaS + CO + Fe.$$

Silicon exerts a marked effect on carbon monoxide, and the products of the reaction are not gaseous, as will be evident from the equation given below; there is then little possibility of the production of steel ingots full of blow-holes as the result of the liberation of carbon monoxide during solidification:

$$2CO + Si = SiO_2 + 2C.$$
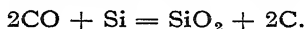
With a very high temperature and slags rich in silica the above reaction may occur in the reverse direction, with the production of high silicon steels which are unsound after casting.

When a good slag is obtained, metal samples are extracted by means of a spoon and cast into small sample moulds, and if the steel is also in good condition it will settle quietly in the mould and be quite sound when the solid sample is fractured. Samples are then drilled and rapidly analysed, the carbon content remaining practically constant. When the analyses are known, calculations are made, and the requisite amounts of the finishing alloys added to the bath. No oxidation allowances are necessary, although there may be a risk of the mechanical suspension of nickel shot in thick slags. The temperature is next corrected, and the contents of the furnace poured into a ladle.

In the Siemens furnace, the metal drains from the bottom of the hearth, and is practically uncontaminated with slag, but in the electric process slag enters the ladle along with the steel, and slag particles may thus be occluded in the metal. Thinning the slag

by the addition of sand just before tilting the furnace has quite a pronounced effect in the promotion of slag flotation. Ferro-titanium is often employed as a final deoxidant in the ladle, and it is also claimed that the titanic acid (TiO_2) thus formed tends to flux out occluded slag particles. During the whole of the de-oxidation period, furnace doors, roof holes, &c., are luted up with ganister in order to exclude atmospheric oxygen and maintain reducing conditions.

Modifications of the Electric Process.

Melting without oxidation is carried out when good clean electric scrap is available, and the composition is suitable for the production of the steel required. This method accelerates the process, and most of the special elements in the scrap are retained in the molten metal; a considerable saving in materials and elec-trical energy is thereby effected, but what is most important, the steels are probably more free from oxide of iron than those made by any other process.

Under these circumstances, practically no slag-making materials, except a little lime, are added until the charge is almost completely molten. Atmospheric oxidation will usually remove the silicon from the charge, but carbon, manganese, chromium, &c., are not effected to any very great extent. When completely melted, more lime along with fluorspar, ferro-silicon, and crushed coal are added in order to yield reducing conditions. Practically all the manganese and chromium which may have been oxidized during melting are reduced and again dissolved in the metal. No slagging operation is performed, since further removal of phosphorus is unnecessary. The method is the analogue of the crucible process, but possesses the additional advantages that desulphurization and perfect deoxidation are obtained. Steels containing large pro-portions of special elements, e.g. high-speed steel, are often made by this process in small electric arc furnaces. In the crucible process an increase in the sulphur content always occurs, whereas in the electric furnace each remelting of high-speed scrap results in a lowering of the sulphur content.

Stainless steel and iron, and the high-chromium heat-resisting steels, are made in comparatively large quantities by this method, but the following methods are sometimes adopted:

(*a*) Low carbon ferro-chrome is diluted with practically pure iron. The desired quantity of very low carbon iron, as determined

by previous calculation, is made from ordinary scrap; good slag and bath conditions are obtained, but slags rich in calcium carbide avoided. The ferro-chrome is then gradually added to the bath, ferro-silicon being added to reduce chromium oxide in the slag. When the bath is completely fluid, the heat is finished in the usual manner.

(*b*) Good ordinary low carbon and stainless steel scrap is melted in the presence of chromite ore, lime, and fluorspar. When a sufficiently low carbon content is obtained, crushed high-grade ferro-silicon and aluminium are added to the slag in order to reduce the chromium oxide added as chromite. In the production of stainless alloys by this process, there is a tendency towards the production of materials rich in silicon, but the process works successfully in the hands of skilled operators.

The Steels produced in the Electric Furnace.

Large quantities of inferior quality steel have been produced in the electric furnace in past years, and particularly during the Great War period, when a large number of furnaces were installed by manufacturers who were not sufficiently acquainted with the technique necessary for the production of good sound steel. Electric steel then obtained a poor reputation, and with some engineers the prejudice against electric steel still persists. The early difficulties have been entirely overcome, however, and steels of the highest quality are now produced, although the process is still by no means fool-proof, and necessitates the services of a skilled metallurgist.

Electric steels have displaced many of those made in the acid Siemens furnace, in particular the high tensile steels used in motor and aero-engine construction, the more complete deoxidation being responsible for the better mechanical properties. Many steels which were essentially products of the crucible furnace are also manufactured in large quantities in the electric furnace. Any comparison of the properties of the steels made by these two processes must necessarily involve some consideration of the size and method of casting the ingots.

In the electric process, the chemical composition of the steel is under more control than in any other steel-making process, and remarkable regularity in composition is obtained. Alloy steels, containing very high proportions of the alloying elements, are made with very little difficulty, the necessary high temperatures

being obtained quite easily. The process is a very flexible one, and nickel and nickel-chrome, ball-bearing, high-speed, stainless, and heat-resisting steels are manufactured in large quantities.

Acid Electric Furnace Practice.

The number of acid-lined furnaces has increased within the last few years, the linings generally consisting of a mixture of sand and ganister rammed into position around wooden templates.

For ingot production, practically the only steels made are those of the high-speed, stainless, and heat-resisting types; the furnace being used as a crucible for melting up specially selected materials. For the production of steel castings, the acid process possesses some advantages over the basic electric process. There is not that necessity for such extreme control, no slag removal becomes necessary, and, in general, the acid process is quicker.

Since no sulphur or phosphorus removal is possible, good quality scrap is essential, although there is no increase in the sulphur content such as occurs when the melting is carried out in crucibles. Low silicon scrap may be charged on to the furnace bed since there is no flame oxidation as in the acid Siemens process.

The acid electric process consists in melting the scrap without much oxidation, sand and broken glass being added, if necessary, to yield a slag covering when a completely fluid bath is obtained. Small feeds of ore are then made until the carbon content is sufficiently low in value; the heat is finished by stewing at a fairly high temperature, and the steel is then poured into ladles.

Deoxidation is not so complete as in the basic electric furnace, but steels of excellent quality, and with any desired degree of fluidity, can be obtained which are most suitable for the production of steel castings.

The High-frequency Electric Furnace.

This is the latest development in furnaces for steel production, and is the most serious rival to the older coke-fired crucible furnace. The high-frequency furnace is a crucible furnace in which the charge is melted by the eddy currents developed in it by a high-frequency current carried by a water-cooled copper coil surrounding the crucible. With small furnaces, a very high frequency is essential, but with increasing capacity much lower frequencies may be employed. A small experimental furnace in one of the research laboratories of the University of Sheffield,

which is capable of melting a few grams of metal only, utilizes a current of 1,500,000 cycles at 7000 volts pressure, and there are several 10-lb. furnaces now running with current of 1,000,000 cycles, whilst the more commercial types, capable of melting up to 1 ton of steel, operate at either 2000 or 500 cycles according to their design.

In the ordinary crucible furnace the crucible is heated before the metal, but in the high-frequency furnace the crucible only becomes hot when it is charged with metallic substances. When the charge has melted, the metal moves in a vertical plane and has a swirling motion imparted to it by the electro-magnetic forces at work. As a consequence of this swirling action, the complete melting and diffusion of heavy elements such as tungsten is obtained, thus yielding homogeneous melts. The furnace is therefore most suitable for the manufacture of high-speed steel.

Stainless irons of very low carbon content may also be made in the high-frequency furnace. For this purpose, the lining is built up *in situ* by ramming ganister around a steel plug. After ramming, the current is switched on and gradually increased The steel plug is thus gradually heated and eventually melts, but long before this occurs the lining has become thoroughly dry and capable of holding the fluid metal. With such a ganister lining, carbon contamination is avoided. Up to the present time the high-frequency furnace is employed solely for melting, i.e. no removal of sulphur or phosphorus is carried out, and the charges consist of specially selected materials such as those employed in the ordinary crucible process.

Steel Ingots—Their Solidification and Associated Phenomena

As already indicated, some steels are cast to a shape which is more or less that of the finished article. In such instances, the properties of the steel are very largely influenced by the conditions under which solidification occurs, and although the mechanical properties may be improved to a very considerable extent by subjecting the materials to some suitable heat-treatment, the best results for many purposes are only obtained on steel which has been mechanically worked previous to heat-treatment. As a consequence, most engineering steels have their origin in the form of ingots, and since the original ingot structure exerts a pro-

nounced influence on the behaviour of the material during forging, rolling, &c., and also influences the properties of the final product, it is important that various phenomena associated with solidification should be considered.

Blow-holes.

After the necessary composition has been obtained, the molten steel must be deoxidized or " killed ", i.e. oxide of iron must be removed, and the amount of dissolved gases so reduced in quantity that these gases, chiefly carbon monoxide (CO), are not present in excess of that required to saturate the solid steel.   Otherwise the excess gas is liberated during solidification, the steel " rises " in the mould, and an ingot is produced which is honeycombed with gas cavities, technically known as "blow-holes".   Such an ingot is commercially worthless (fig. 13, facing p. 24).   Blow-hole formation is prevented by the addition of alloys known as deoxidants such as ferro-manganese, ferro-silicon, ferro-titanium, and aluminium. All these alloys react with ferrous oxide, which is soluble in steel, to yield insoluble oxides, and these enter the slag.   According to McCance,* steel cannot be perfectly deoxidized by manganese or silicon alone, and in practice both elements are generally present in the steel in the later stages of any process; and in most instances also a small quantity of aluminium is added just before the metal is poured into the ingot moulds.   Aluminium exerts a powerful action on dissolved gases, and in most cases the addition of such a small amount as 0·02 per cent of the element suffices for the production of sound steel ingots perfectly free from blow-holes, provided that a fair percentage of manganese is also present. There is one great objection to the use of aluminium when the element is employed in the production of steels which have highly polished surfaces in the finished condition, e.g. ball-bearings, razor blades, &c.   " Specks " of alumina (Al_2O_3) may show up on the surfaces of the finished articles, and so killing solely by aluminium is only applied to high-carbon steels which require an extremely keen cutting edge.

Blow-holes in steel ingots may be either *subcutaneous* or *internal*. Internal blow-holes are formed in the interior of the ingot, and their surfaces are generally silvery-white in appearance.   Subcutaneous blow-holes are found just under the skin, and their walls are often coloured owing to thin oxide films.

* *Trans. Faraday Soc.*, Vol. XXI, 1925.

Internal unoxidized blow-holes may weld up during forging, but the oxidized subcutaneous blow-holes never do so, but become elongated and give rise to the production of superficial " rokes ". The fine " hair-lines " observed on finished polished surfaces can often be traced to subcutaneous blow-hole formation in the ingot. High-quality steels should be entirely free from blow-holes of any description.

Low carbon steels for sheet and plate manufacture are often intentionally semi-killed, although the metal is not really badly oxidized, and the extent to which the ingot rises after casting is carefully controlled. Such products are known as *rimming* or *effervescing steels*, and are full of internal blow-holes, but practically free from pipe. The impurities are therefore evenly distributed, since the structure generally consists of small " equiaxed " crystals (fig. 13, facing p. 24), and the blow-holes weld up more or less completely during rolling.

Pipe in Steel Ingots.

As the steel solidifies in the mould, freezing occurs first of all on the outside surfaces, and the thin shell so formed obviously determines the shape and, to a great extent, the size of the resulting ingot. Solidification is, however, accompanied by contraction, and the last material to freeze fills up only part of the space left by the contraction of the main mass; so that unless precautions are taken to prevent it, the solid ingot will have a section represented in fig. 14. The contraction cavity thus formed is known as a " pipe ", the extent of which is influenced by several factors. High carbon steels tend to pipe to a very great extent if cast at very high temperatures, and more particularly if containing high percentages of silicon or alu-

Fig. 14.—Longitudinal Section through " Piped " Ingot.

minium. Any portion of an ingot which is piped is waste and should be rejected; otherwise the pipe is drawn out during forging and rolling, and the resulting bars will tend to split either during working or during any subsequent hardening operation. The above effect cannot be entirely eliminated, but the ill-effects can be minimized in the case of small ingots such as those made by the crucible and high-frequency furnace processes by using a short fireclay cylinder, known as a *core* or *dozzle*,
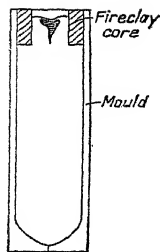
Fig. 15.—Showing Effect of Core on Pipe-formation in Steel Ingots.

which has for its external shape that of the interior of the mould. When all but a few pounds of the steel has been poured into the mould, the red-hot core is inserted and filled with the liquid metal remaining. The steel in the core, by virtue of the poor thermal conductivity of the fireclay, is retained in a molten state for a much longer time than that in the ingot proper, and this fluid material thus acts as a reservoir and serves to fill up any contraction cavity formed by the solidification of the main mass. By this means the pipe is formed in the core and not in the ingot, the amount of waste material being thus reduced from about 30 to 3 or 4 per cent (fig. 15).

Influence of Shape of Mould on Pipe.

Most Siemens and electric furnace steels are of comparatively low carbon content and do not pipe to quite the same extent as the higher carbon steels. At the same time, however, it is important that precautions should be taken to minimize pipe in the ingots produced by these processes. These ingots are usually much larger, and the larger ingot moulds are generally rectangular in cross-section, with rounded corners, and taper slightly so as to facilitate withdrawal of the ingots after casting.

Hexagonal and circular moulds are sometimes employed. Cylindrical ingots possess the advantage that surface defects may be easily turned out on the lathe, but they require careful treatment during forging, since axial cracks readily develop. Large ingot moulds are generally open both at the top and the bottom, heavy base plates closing the lower end during casting operations.

In a mould which is wider at the bottom than the top, the freezing and contraction of the metal may result in a cavity low down in the ingot known as a "*secondary*" *pipe* (fig. 16 (*a*)). This may escape detection during working, and afterwards gives rise to trouble. By using moulds with the wide end at the top, secondary pipe formation is minimized even if it is not entirely eliminated. In addition, the ordinary or "*primary*" *pipe* is more squat and does not extend nearly so far into the ingot. The pipe can be lessened to a still further extent by using refractory-lined boxes known as *feeder-heads* (fig. 16 (*c*)). These are placed on top of the moulds, and when filled with molten metal serve the

Fig. 17.—Slag inclusions in the vicinity of the piped portion of a broken crankshaft. Note the almost carbonless areas or ghosts around the slag particles. × 50.
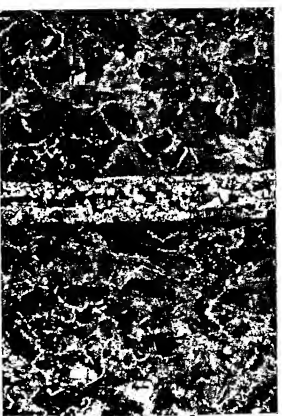

Fig. 18.—Part of pipe in tensile test-piece which broke without any elongation

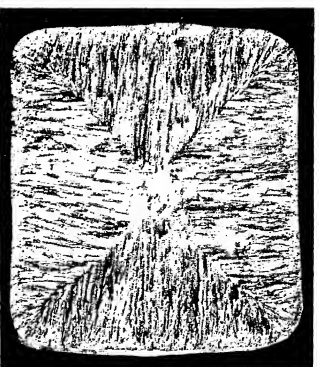Fig. 19.—Sections of steel rod showing segregated centre. (a) Actual size. (b) Main metal. × 200. (c) Centre. × 200

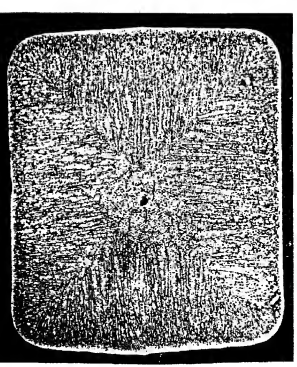Fig. 20.—Fractured surface of ingot cast at much too high a temperature, long columnar crystals extending nearly to the centre.

Fig. 21.—Polished and etched surface of ingot cast "too hot"

same purpose as the cores in crucible practice. By these means, the whole of the pipe is generally confined to the feeder-head.

Since the material in the vicinity of the pipe is the last to freeze, this region is richest in the impurities, sulphur and phosphorus, and many slag particles are occluded. Carbon segregation may also occur to a very marked extent, although some diffusion of the element does occur when the ingots are reheated. Piped portions of an ingot should always be discarded. Phosphorus displaces carbon in solid solution, and if much segregation occurs the vicinity of the piped portions may be almost carbonless. Such areas are often referred to as *ghosts* (figs. 17 and 18).
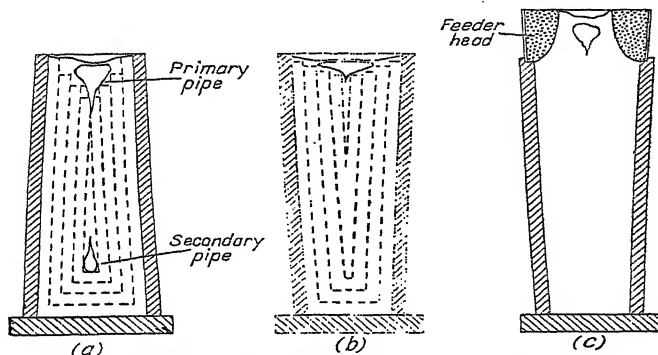

Fig. 16.—Illustrating Effect of Feeder-head and Shape of Mould on Pipe

If the pipe is to be confined to the feeder-head, it is essential for the metal in the head to remain quite fluid when practically the whole of the ingot has solidified; and in order to maintain this fluidity the surface is sometimes covered with hot coke or charcoal. The molten metal then rapidly absorbs carbon, however, and if the ingot pipes to any marked extent diffusion of this carbon may extend far down the centre of the ingot. The centres of finished materials may then contain much more carbon than the remainder. Something of this nature was evidently the cause of the segregated centre of the rod shown in fig. 19 which cracked when hardened. The material was supplied for a 0·55 per cent carbon steel, but although the average carbon content was only 0·62 per cent, the centre is of eutectoid (0·9 per cent) composition.

The Influence of Casting Temperature on the Properties of Steel Ingots.

The temperature of casting exerts a marked influence on the properties of the ingot and also on those of the finished product.

Freezing commences on the outer surfaces; the crystals thus formed then grow inwards perpendicular to the faces of the mould, and in so doing, tend to drive the impurities and occluded slag particles before them. When the temperature of casting is very high, long columnar crystals may extend to the centre of the ingot (figs. 20 and 21, facing p. 52), most of the impurities then being distributed along the axis. The axial or "*major*" *segregation* then obtained persists in the finished articles, and although the average composition may be within specification limits, localized areas are obtained in which the impurities, chiefly sulphur and phosphorus, greatly exceed the specified values.

Axial segregation gives rise to the formation of internal flaws and "cuppiness" in wire-drawing, and in heat-treated materials cracks may develop during quenching.

Crystallization also proceeds from the bottom of the mould, and the junctions of these crystals with those growing from the faces constitute pyramidal planes of weakness due to the impurities entrapped and contained therein. Difficulties are then encountered in forging, as the ingot may readily split along the pyramidal planes. With an ideal casting temperature, freezing of the whole ingot occurs more quickly, and the columnar crystals do not extend so far into the ingot. The interior, and by far the larger mass, then consists of small "*equiaxed*" *crystals* (fig. 22), throughout which the impurities are more evenly distributed. The ingots forge quite satisfactorily, and as the result of considerable steel-making experience the author is of the opinion that the ingots should be cast at as low a temperature as is consistent with the necessary degree of fluidity. Steels cast at very low temperatures, however, and particularly when cast from the bottom upwards, give rise to "lapped" ingots (fig. 23). As the metal rises in the mould, a semi-solid skin forms on the surface through which the fluid metal periodically bursts. The skin oxidizes, and the oxidized surface is covered over by the rising fluid. The ingots
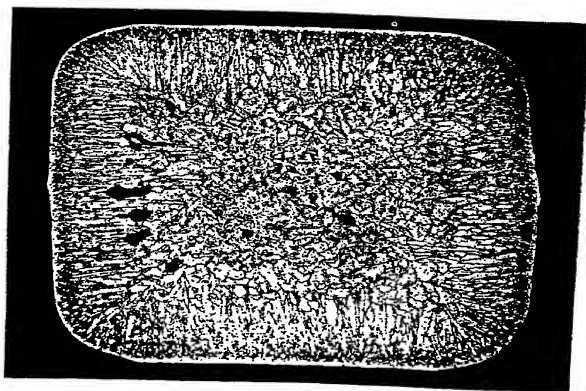
Fig. 23.—Illustrating "Laps" on Ingot Surface.

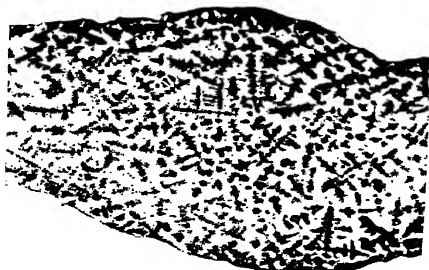Fig. 22.—Polished and etched ingot section showing both columnar and equiaxed crystals

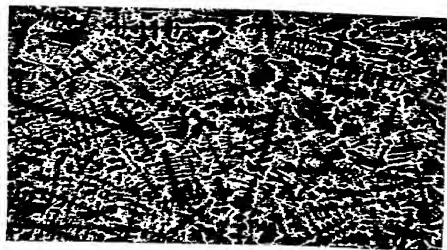Fig. 25.—Large dendrites in Ni-Cr steel ingot. ×3.
Etched with Oberhoffer's reagent

Fig. 26.—Dendritic structure in 3½ per cent Ni steel. ×10.
Etched with Oberhoffer's reagent

may forge and roll without difficulty, but the oxidized surfaces become elongated into " rokes ". These may lead to the formation of cracks during heat-treatment, and also tend to diminish the fatigue-resisting properties of the material. Rokes and surface cracks exert a much more harmful influence on the properties of such steels than does axial segregation.

Major segregation in an ingot is very rarely truly axial, but is more often revealed by marked lines having a pronounced upright or inverted V-shape, which show up when the ingots are sectioned axially and then suitably etched (fig. 24, facing p. 56). This form of segregation is particularly troublesome in ingots containing appreciable amounts of impurities, since, during working, the segregates become flattened and elongated, the centres of finished articles then containing a proportion of impurities greatly in excess of stipulated values. Both V- and Λ-segregation are influenced by the taper of the mould, but there is little doubt that the temperature of casting exerts a marked influence on both types, which are much less marked when lower casting temperatures are employed.

High casting temperatures also yield coarse *dendritic structures*, particularly in nickel and nickel-chrome steels (figs. 25 and 26). Nickel diffuses slowly in the solid state, and the heterogeneity of structure due to these dendrites persists to a great extent, even in the finished products. Further, during solidification, impurities are also entrapped between the arms of neighbouring dendritic crystals. This gives rise to what is known as " *minor* " *segregation* which is accentuated by a high casting temperature. This minor segregation may also be accompanied by local carbon segregation, with the consequence that in some of the alloy steels minute areas having a very pronounced air-hardening tendency may be present in what is otherwise a pearlitic steel exhibiting little or no tendency to air-harden. The difference in the volume changes which occur between these areas and the main mass during cooling of the ingot then results in the production of internal unoxidized cracks known as *flakes* or *snowflakes*, so called because they exhibit a white flaky appearance when the steel is fractured. This defect is peculiar to alloy steels, and may cause the steel to fracture when heat-treated. In addition, flakes may also appear as lines on the finished machined or polished surfaces. This difficulty is apparently completely overcome by careful control of the casting temperature and slow cooling of the ingot after solidification is complete.

Methods of Casting.

In casting steel ingots, the moulds may be filled from either the top or the bottom. In the latter case, the metal is poured down a central fireclay pipe and then flows along radial fireclay " runner " bricks into the bottom ends of several moulds, from four to eight of these being filled simultaneously. This method possesses several advantages over the " top-casting " method. When top-cast, some of the metal is splashed up the sides of the mould. The splashings adhere to the sides, and are quickly chilled. Oxidation then occurs, and the solid particles are never completely taken into solution by the rising liquid. The liquid surface is also violently disturbed, and these two factors contribute largely to the production of bad surfaces on the ingots. Forged " billets " and rolled blooms then require careful inspection for rokes.

In order to minimize splash, the " tundish " is frequently used. This is a refractory-lined box having a ladle nozzle in the bottom. The nozzle generally has a lesser diameter than the ladle nozzle. The tundish is placed on top of the mould or feeder-head and acts as a secondary ladle, in which, however, the head of metal is greatly reduced. The pressure at which the molten steel enters the mould is therefore lessened, and the effects of splash are confined to the lower surfaces of the ingot.

In bottom casting, splash is prevented; the surface of the fluid metal in the mould is disturbed to a lesser extent, and what is perhaps of much greater importance, the casting temperature of the whole charge is rendered much more uniform. From the steel-makers' view-point, bottom casting is also advantageous, since the ladle nozzle is not closed so frequently, as sometimes the fireclay nozzles and stopper ends are not refractory enough and tend to adhere when the ladle stream is cut off. In such cases, the metal remaining in the ladle must be poured over the lip, a most unsatisfactory procedure in view of the fact that the ingots so produced are liable to contain abnormal quantities of slag.

Bottom casting has one rather serious disadvantage. Fluxing of the runner bricks may occur, and thus increase the proportion of non-metallic inclusions in the ingot. The effect is more pronounced with high casting temperatures, but with careful control the ill-effects due to this source can be rendered almost negligible.
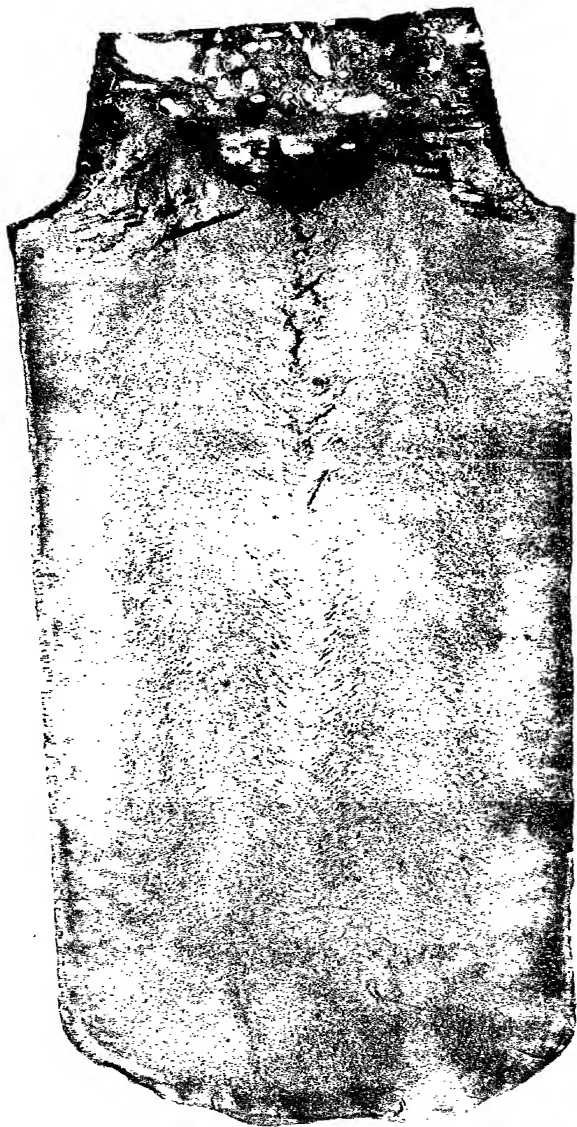
Fig. 24.—Photograph of sulphur print of 2-ton ingot.
V-segregates clearly shown. Approx. ½ actual size

Slag Inclusions.

Non-metallic inclusions in steel are a constant source of trouble. In crucible steel-making, the slag is small in bulk, and is easily removed before or whilst the steel is being poured into the mould. In the Bessemer, Siemens, and electric arc furnaces, the slag is large in bulk, and, as already indicated, is retained in the ladle by allowing the steel to flow through the hole or nozzle in the ladle bottom. Even then, slag particles may be held in suspension in the fluid metal, and in many cases are entrapped in the solid ingot.

Tilting furnaces are particularly liable to yield steels containing abnormal quantities of occluded slag particles, owing to the vigorous agitation and mixing of the slag and metal in the ladle. Most of the slag can be held back by placing a rabble across the surface of the molten stream as it issues from the furnace.

If they are present in a small proportion only, and are evenly distributed, slag particles are not particularly detrimental for ordinary purposes, but " dirty " steels containing abnormal amounts are a common cause of failure. Slag particles will initiate corrosion, and, even in the so-called stainless steels and alloys, once this commences, the whole surface may be rapidly attacked. The author examined samples of stainless iron which " pitted " badly when pickled, and gave a poor surface after polishing. The material was made in the Héroult electric arc furnace, and, apart from containing numerous minute particles of slag, was of excellent quality as regards chemical composition, microstructure, and mechanical properties.

Many steel-makers allow the steel to remain in the ladle for a short time before pouring it into the moulds. Slag particles are then allowed a better opportunity of rising to the surface, and the proportion of non-metallic inclusions in the ingot is considerably reduced.

Cracks.

Cracks may sometimes develop in steel ingots during cooling, particularly after casting at high temperatures, and may be either transverse or longitudinal. The latter are generally due to uneven cooling after removal from the moulds, whilst bad moulds having uneven surfaces may give rise to both types.

Badly fitting feeder-heads lead to the formation of transverse

cracks near the head of the ingot. The metal forces its way between the feeder-head and the mould, and the solid flange so formed resists the normal contraction on cooling. Some of these cracks may escape detection in the forge, and unsound roky billets are thus produced.

The speed at which the steel is cast also has some influence on crack formation. If cast too quickly, cracks may develop on cooling, and an exaggerated pipe be obtained, whilst if the casting speed is too slow, lapped ingots are obtained.

The distribution of the impurities in steel is revealed by (a) analyses of various portions of the ingot, (b) sulphur printing, and (c) macro-etching.

Sulphur Prints.

A sheet of bromide paper, after being soaked in dilute sulphuric acid, is placed on the plane polished surface to be examined, air-bubbles being eliminated by rolling with a squeegee. The concentration of sulphuric acid required depends somewhat on the composition of the steel, but in most cases solutions of about 5 per cent strength give satisfactory results. The manganese (and iron) sulphide reacts with the acid to liberate sulphuretted hydrogen, which acts on the silver salt in the paper to give a dark-brown stain of silver sulphide. After a short time, the paper is stripped off, washed with water, and then fixed in " hypo " solution. The prints really only indicate the distribution of the sulphur, but since the other impurities are generally segregated with it, they serve as an index to the distribution of them all.

Macro-etching.

For deep etching, the prepared surface is attacked with either 10 per cent nitric acid or one of the many copper reagents. Humfrey * has recommended the following solution:

> Copper ammonium chloride, 120 grams.
> Concentrated hydrochloric acid, 50 c.c.
> Water, 1000 c.c.

It is advisable to commence the attack with a neutral solution of the copper salt, otherwise some difficulty may be encountered in removing the copper deposit. The duration of the etch depends on the composition of the steel, and is best found by trial. The

etched surface is then thoroughly cleaned with hot water and rubbed with cotton-wool to remove the copper and deposited carbides, and finally cleaned and dried with benzol. If the surface is then lightly rubbed with No. 0 emery paper, the structure is more clearly defined. The surface may then be photographed, but more often macro-prints are obtained by covering the surface with a thin layer of printers' ink, evenly applied by means of a squeegee, and transferring the pattern on to " glossy art " paper. The paper is placed on the inked surface and gentle pressure exercised by a clean dry squeegee.

Macro-prints are useful in revealing ingot structures, and are invaluable in showing the " flow " of forged and rolled articles. Dendritic structures are also beautifully revealed by etching the highly polished surfaces with Oberhoffer's reagent (figs. 25 and 26), which consists of:

Ethyl alcohol, 500 c.c.	Stannous chloride, 0·5 gram.
Water, 500 c.c.	Ferric chloride, 30 grams.
Copper chloride, 1 gram.	Conc. hydrochloric acid, 50 c.c.

When etched with this reagent the dendritic structures may be photographed in the usual manner.

The Hot-working of Steel

The primary object of mechanical treatment is to obtain the steel in the desired size and shape. The modification of structure which is brought about by hot-working is of greater importance, however, in view of its influence on the mechanical properties Steel, in general, is weak in the cast state, and although an improvement in properties is obtained by annealing, mechanical work must also be applied to most steels in order to obtain the necessary toughness.

Working yields smaller grains and greater uniformity of structure by breaking up the original dendrites. The broken and distorted dendrites constitute the grain or fibre of forged and rolled steels. To work the material satisfactorily, it must be reheated to a temperature well within the solid solution region. This temperature is generally above 1000° C., and the internal viscosity is then reduced to such an extent that the steel is plastic and readily yields to the forces applied to it.

The higher carbon steels require extremely careful treatment, and must not be heated to such high temperatures as the lower

carbon steels, since otherwise the treatment tends to produce excessive decarburization. High carbon steel ingots should be reheated in a non-oxidizing atmosphere, i.e. a "smoky" flame should be employed, and the ingots turned over at intervals. All steels should be slowly heated and thoroughly soaked before work is commenced.

High carbon steels and many alloy steels are often rolled to finished size after forging.

Forging.

Forging may be done under either the hydraulic press or under a steam or pneumatic hammer.

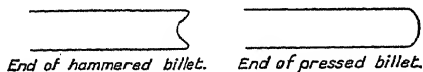Hammering gives uniformity of structure, and is always applied to high carbon, high-speed, and many alloy steels. In hammering, the effect of each blow should penetrate to the interior, otherwise more or less of the brittle cast structure is retained. A succession of light blows merely works the

End of hammered billet.   *End of pressed billet.*

Fig. 27.—Showing Effect of Forging on the Ends of Forged Billets

outside layers. Thorough soaking in reheating is essential, otherwise the material has not the necessary plasticity, internal cracks may be formed, and the forging is hollow.

Hammering does not affect the interiors of large masses to a sufficient extent, and the necessity for working the interiors of large ingots led to the introduction of the hydraulic press in which the ingots are squeezed. The press maintains a steady pressure, and kneads the metal like dough. The difference between hammered and pressed billets is often evidenced by the appearance of the ends (fig. 27).

Hammering affects the surface to the greater extent, but with the press more flow occurs in the interior. Small ingots such as those used for the higher carbon and high-speed tool steels are better hammered, as this breaks up the structure better than the press. With the larger ingots, the time taken in reheating and soaking is longer, and there is the possibility of the formation of a heavy covering of scale. Hammering tends to knock the scale into the ingot, and better surfaces are generally obtained on the billets by means of the press. The changes in structure induced by forging are illustrated in figs. 28, 29, 30, and 31.

Fig. 28.—3¼ per cent nickel steel in cast state. ×250. Note the heterogeneity of structure.

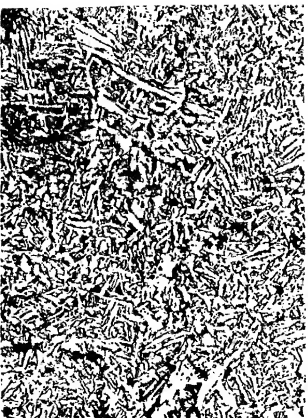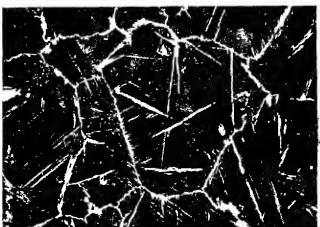Fig. 29.—Same steel as fig. 28, but in the forged condition. ×250. Structure finer and more homogeneous.

Direction of rolling →

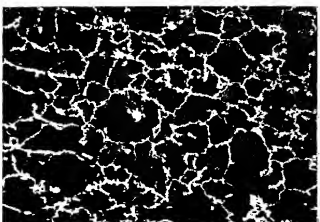
Fig. 30.—Razor steel containing 1·3 per cent C in the cast condition. ×100.

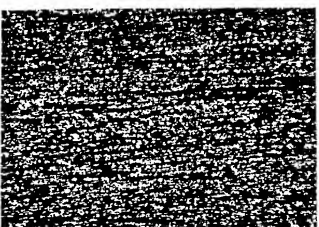Fig. 31.—Same steel as fig. 30, but in the forged condition.

Fig. 32.—1·3 per cent steel, forged and then rolled: longitudinal section. ×100. Cementite and pearlite.

Fig. 33.—Steel containing 0·25 per cent C, 0·75 per cent Mn: longitudinal section as rolled. ×75. Ferrite and pearlite.

Rolling.

Rolling is carried out more cheaply than forging, and for many purposes the bars produced are quite satisfactory. Some steels are therefore rolled directly from the ingots. These steels yield
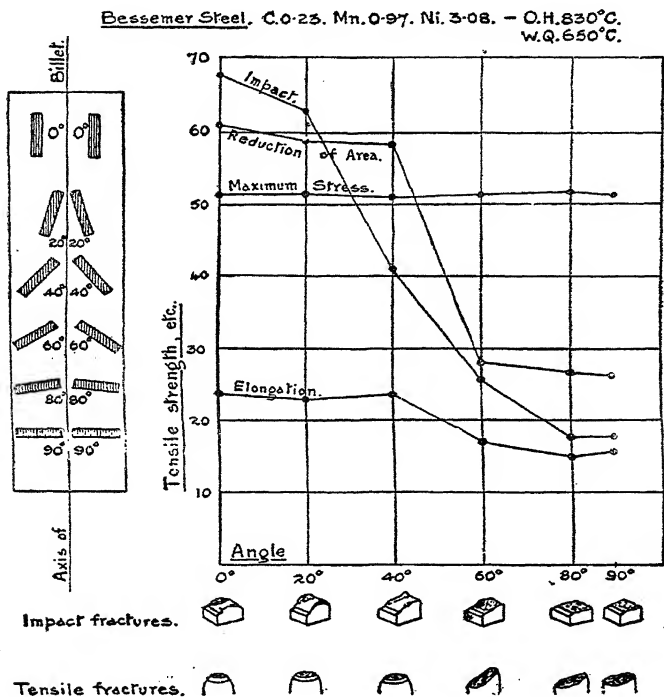

Fig. 34.—Influence of Slag Lines, &c., on Steel, showing their Effect in relation to the Direction of Stress (Brearley)

microstructures showing the various constituents in elongated forms and apparently drawn out in the direction of rolling (figs. 32 and 33).

Dendrites, which are formed during solidification of the ingot, are never entirely eliminated, but are distorted, and in rolled steels are drawn out during rolling. The impurities—slag particles, man-

ganese sulphide, &c.—which are entrapped between the dendrites, are drawn out into threads, and when the steel cools the excess ferrite (or cementite, depending on the carbon content) is deposited around these impurities. This accounts for the production of the above structures, which together with the disposition of these impurities, greatly influence the properties of the material in different directions. This influence is illustrated in fig. 34, the result of tests carried out by Brearley. The diagram shows that although the maximum stress and elongation per cent remain more or less constant, the reduction of area per cent, and in particular the impact values, are subject to very considerable variation. These effects are likely to be more pronounced with steels cast at very high temperatures, but with a correct casting temperature the structure and properties are more uniform.
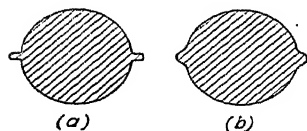

(a)   (b)

Fig. 35.—Illustrating the Formation of "Fins" on Rolled Rods

In rolling, the hot steel is passed through flat or grooved rolls according to the cross-section required. When finishing round sections, the groove is not truly circular. This is to avoid the formation of sharp " fins " (fig. 35 (a)), but even then, fins of the shape shown in (b) are formed, although these are eliminated by turning the bar or rod through 90° and re-rolling through the same groove. Fins may give rise to "lapped" rods and wires, and extreme care is essential in designing the rolls in order to avoid the formation of fins which are too pronounced. The chief point in design is so to shape the passes that no two consecutive passes tend to form fins in the same relative position of the bar, but that the fins formed in one groove are rolled out in the next. The cross-section at each pass is therefore generally different in shape from its predecessor and the one following. By this means, work is put upon every part of the bar, and in addition the material can be drawn down at a greater speed. By alternate ◆ and ● grooves, for finished circular rod or wire, the section can be reduced by as much as 50 per cent at each pass.

Drop-forging.

High-quality steels are better forged and then rolled, but for some purposes the articles are better finished by drop-forging The steel is forged under a hammer die, the face of which has been
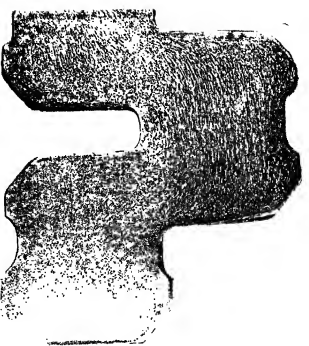
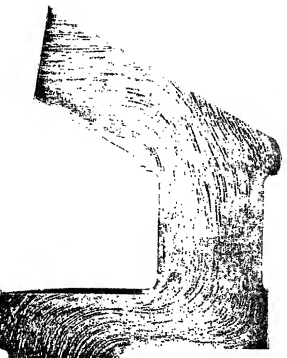Fig. 36.—Macro-etched surface of a good drop-forged crankshaft. Reduced by half.

Fig. 37.—Drop-forged crankshaft—not quite so satisfactory as that of fig. 36; grain rather too pronounced and flow does not follow change in section as completely as it might do.

Fig. 38.—Macro-print of axle turned from cylindrical bar
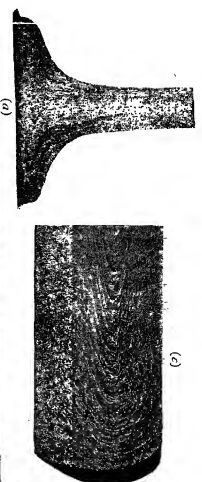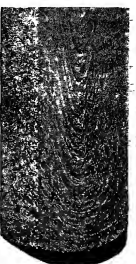
Fig. 39.—Showing flow of grain in up-ended articles
(a) Macro-etched section of valve—actual size—flow almost ideal.
(b) Macro-print of pinion forging—good structure.
(c) Etched section of gear blank—slightly reduced—structure not so good as desirable.

Fig. 41.—Head of broken bolt showing burnt structure. × 100

Fig. 42.—Threaded end of bolt shown in fig. 41: coarse overheated structure. × 100

machined so as to give, together with that of the block, a more or less finished shape to the forging.   Drop-forging reduces machining costs, and also gives a better flow of the grain 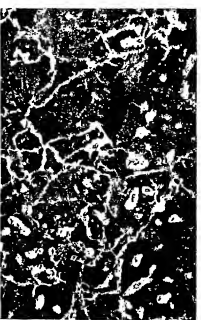in the finished articles.   The correct grain is not obtained at one operation, but the final shape is generally produced after several reheatings.   The design of the dies, by means of which the shape of the forging is gradually altered, calls for much skill and experience.

The grain of a good drop-forged crankshaft is shown in fig. 36, and this should be compared with those in figs. 37 and 38.

For many engineering purposes, steels with the least developed grain should be selected, and failing this with the grain in such

Gear made from Round Bar   Gear made from Flat Bar   Gear made from Up-ended Bar
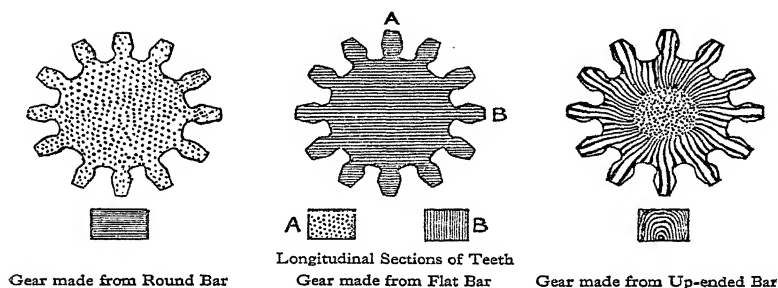
Longitudinal Sections of Teeth

Fig. 40.—Showing "Fibre" in Teeth of Gears made by Different Methods

direction that it is least harmful.   In order to obtain fibre which is most favourably disposed, many articles are "up-ended", i.e. knocked up from a smaller to a larger diameter.   These effects are illustrated in fig. 39 (*a*), (*b*), and (*c*).

Blanks for gears, milling cutters, &c., are sometimes cut from round bars or even from flat slabs.   In either case, the grain is least favourably disposed to the working stresses as illustrated in fig. 40.   Up-ending adds to the cost of production, but yields a material which is more reliable.

Bolt-heads are sometimes formed by up-ending in order to obtain the desired flow of the metal in the head.   With such small articles, there is a risk of the material being "over-heated" or even "burnt".   When burnt, incipient fusion of the steel occurs, and the material is exceedingly brittle.   Figs. 41 and 42 are from the head and threaded portions of a bolt, the head breaking off

in service. The micrograph shows the burnt structure, and that of the screwed portion indicates overheating.

The section of a burnt forging is shown in fig. 43. This was a large drop-forging made in two parts; during the reheating for the second part, that already finished, being of smaller cross-section, was overheated and burnt. Fatigue cracks subsequently developed and ultimately resulted in failure.
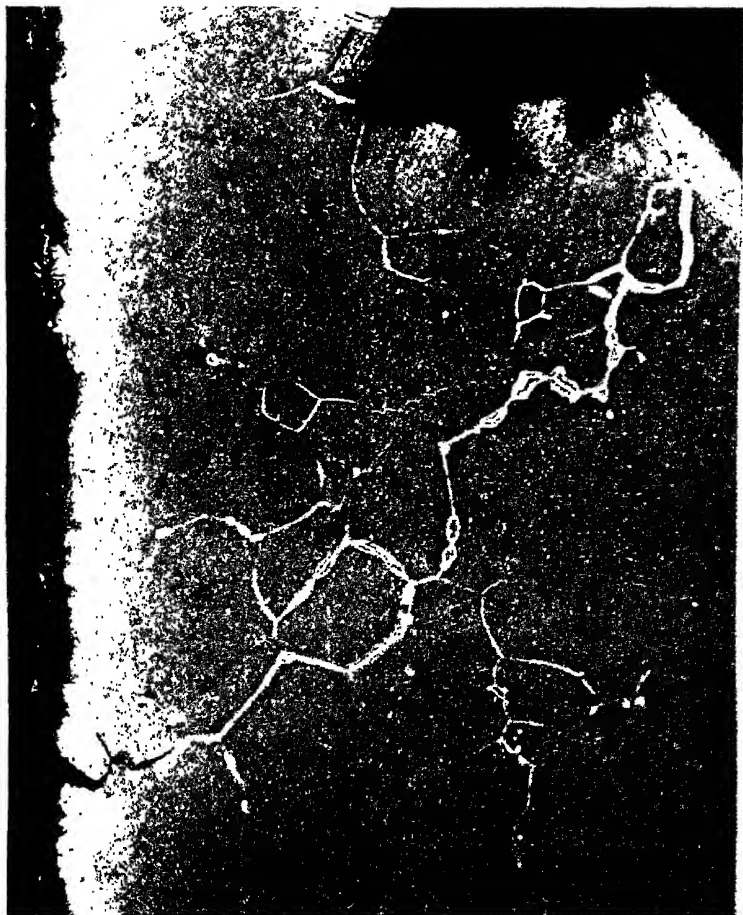
Fig. 43.—Fatigue cracks in burnt drop-forging.   × 15

CHAPTER III

The Constitution of Metallic Systems

Solutions.

Pure metals are not employed to any great extent in engineering, the more useful engineering materials being alloys, i.e. mixtures of two or more metallic substances.

These alloys are generally molten at some stage in manufacture, and a very close analogy exists between such liquids and ordinary solutions.

When crystals of a solid are shaken up with a suitable solvent, the solid disappears. During the process of solution a definite pressure is exerted, which is known as the osmotic pressure, and the experimental laws concerning this pressure, deduced from the examination of the properties of solutions of non-electrolytes, are strictly analogous to those derived from the study of gases.

It seems logical, therefore, to assume that the substance is converted, during solution, into a state comparable with the gaseous state. Gases diffuse rapidly, and, in many instances, the rate at which the particles of a dissolved substance diffuse throughout the solvent is such that homogeneous solutions are readily obtained. The homogeneity of a true solution which is coloured is obvious, and, although the homogeneity is not so readily apparent in the case of colourless solutions, this fact is definitely established by physical and chemical means. In most instances, the dissolved substance is easily recovered by the evaporation of the solvent.

In the extraction process for gold the metal is dissolved in mercury, and in the assay of gold ores is dissolved in molten lead. In the first case, the gold is recovered by a true process of evaporation by distillation of the mercury, and in the other, the lead is removed by cupellation, the pure gold remaining behind in both instances. Now the melting-point of gold is 1061° C., and in neither process is the temperature anything like so high as this.

These liquid solutions of metals are thus comparable with ordinary solutions.

Besides solutions of solids in liquids, several other kinds of solution are possible. Thus there may be:

(*a*) *Solutions of gases in each other*: the particles of mixed gases readily interdiffuse, and the resulting mixtures are perfectly homogeneous;

(*b*) *Solutions of gases in liquids*: gases such as nitrogen and oxygen are soluble in water, from which they are readily expelled on boiling;

(*c*) *Solutions of gases in solids*: certain metals are capable of absorbing gases; thus palladium readily absorbs hydrogen, and there is abundant evidence to show that the gases—carbon monoxide, nitrogen, and hydrogen—are soluble in solid iron;

(*d*) *Solutions of liquids in liquids*: alcohol and glycerine, when added to water, dissolve to yield homogeneous solutions;

(*e*) *Solutions of solids in solids*: this phenomenon is readily demonstrated by firmly riveting a thin sheet of copper between two thicker sheets of iron. On heating, but to a temperature much below the melting-point of either metal, diffusion in the solid state occurs, and, on cooling, the layer of copper is no longer observed. The metal has dissolved in the iron to form a *solid solution*. Such solid solutions are of extreme practical importance, and many are formed by the addition of a solid metal of higher melting-point to one which is already molten. Under such circumstances, in many instances, the crystals which are deposited during freezing are not pure metals but solid solutions.

Copper has a melting-point of 1083° C., but readily dissolves in molten silver below 1000° C. The addition of small amounts of copper gives no separation into parts when the metal is solid, and the alloys are quite homogeneous when examined under the microscope, e.g. silver coinage consists of a series of homogeneous crystals.

In many cases, the addition of one metal to another lowers the freezing-point of the solvent metal, and analogous changes also occur in the solid state. This again is strictly comparable with ordinary liquid solutions, as given by Raoult's law for the depression of the freezing-point of a solvent by a solute.

It is thus clear that alloys give rise to the formation of true solutions in both liquid and solid states, and hence some know-

ledge of solutions and solution phenomena is necessary in the study of metallic systems.

Thermal Phenomena pertaining to Solution.

If the assumption that the particles of a dissolved substance are converted into some state comparable with the gaseous state be valid, the process of solution would be expected to involve some energy change. Thus, when many salts are dissolved in water, the heat of solution is extracted from the water itself, and the temperature of the solution is lowered. Freezing mixtures owe their efficacy to this phenomenon.

The addition of tin to mercury will lower the temperature to such an extent as to freeze any moisture on the outside of a glass containing vessel.

The reverse effect, that is, the liberation of heat during re-crystallization, is not so easily demonstrated, although it is readily shown with some supersaturated solutions. A supersaturated solution of ordinary photographic hypo in water will crystallize spontaneously when the solution is inoculated with a very small crystal of the salt, and a considerable rise in temperature occurs.

Unsaturated, Saturated, and Supersaturated Solutions.

A solution is defined as a physically homogeneous mixture, the composition of which may undergo continuous variation within certain definite limits. Between these limits the solution is *unsaturated*, since it is still capable of taking up more of the dissolved substance. Thus a solution of potassium chloride in water is a homogeneous liquid which may contain from 0 to 34 per cent by weight of potassium chloride at 20° C., but not more than 34 per cent, since this is the maximum amount of salt which will dissolve in water at this temperature. A solution containing this quantity, in contact with undissolved solid potassium chloride, is therefore a *saturated* solution.

If the temperature of the solution is raised, however, the solubility of the potassium chloride increases, but again there exists a certain maximum concentration corresponding with any definite temperature whereby one homogeneous saturated solution is formed. By plotting these maxima against temperature, a solubility curve is obtained. The solubility of most substances increases as the temperature rises.

When a solution which is saturated at a higher temperature is

allowed to cool, the excess of the dissolved substance is usually deposited during cooling. Under some circumstances, however, this deposition does not occur, and the solution at lower temperatures then contains more of the dissolved substance than is indicated by the solubility curve. Such a solution is said to be *supersaturated*. Supersaturated solutions, from which crystals separate when a fragment of the solid phase is added, are in a condition of metastable equilibrium; and in many cases supersaturation is avoided by either stirring or inoculation with some minute amount of solid matter.

Both liquid and solid solutions exhibit this phenomenon. The formation of unsaturated, saturated, and supersaturated solutions is dependent entirely on temperature. A saturated solution may become unsaturated at a higher temperature, but on cooling below the initial temperature this same solution may become supersaturated.

Mixtures of Liquids.

Mixtures of liquids, including mixtures of liquid metals, may be classified as follows. Thus the two liquids may be:

(*a*) Insoluble in each other;

(*b*) Partially soluble in each other, in which case there is a definite limit to the solubility; or

(*c*) Completely soluble in each other in all proportions.

It is probable that no absolute case of (*a*) exists, although lead and aluminium, during constant stirring, form what is really an emulsion which on standing separates into two distinct layers, and the analysis of the two solid layers shows practically pure lead and pure aluminium respectively. In such cases, the freezing of one metal is entirely unaffected by the other, and the condition of any mixture of the two metals at any temperature may be represented by such a diagram as fig. 44, where concentration has been plotted against temperature.

The difference between (*b*) and (*c*) above is really due to temperature alone, and the case of partial solubility will therefore be discussed. Mixtures of phenol and water furnish a good example of the case of partial or limited miscibility.

If at some definite temperature lower than 68·3° C. phenol is added crystal by crystal to water, it dissolves to yield a homogeneous liquid, but eventually a point is reached at which the

water becomes saturated and the next crystal of phenol does not dissolve. It does not remain as phenol, however, but dissolves water from the saturated " aqueous " solution already formed, which results in the formation of a second saturated solution which grows in bulk as more phenol is added. Two distinct liquid layers are then obtained, but as still more phenol is added, one solution is again obtained, this time, however, a solution of water in phenol.

If the saturation values for water in phenol and phenol in water are determined for a series of temperatures, and the data thus obtained are plotted, a curve of the type shown in fig. 45 is obtained.
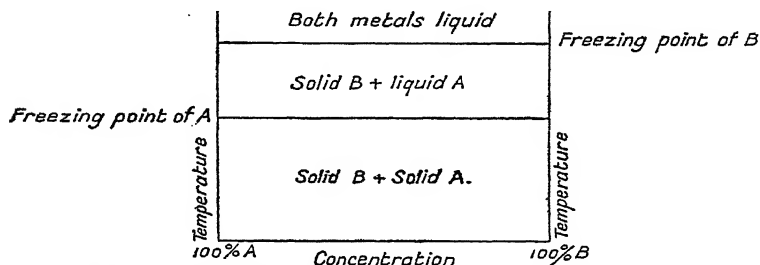

Fig. 44.—Thermal Diagram for Substances completely Insoluble in each other

Consider a mixture of the two liquids represented in composition by the point x and at a temperature $t_1°$ C. The solution is unsaturated, but on adding more phenol and maintaining a constant temperature, the concentration of the solution gradually increases until the point on the solubility curve is reached where the water becomes saturated with phenol. The composition of this saturated solution is represented by x_1. On adding more phenol, a second saturated solution is formed with a composition represented by x_2, and with still more phenol, this second solution, although still retaining the same composition, grows in bulk at the expense of the solution of composition x_1. Such solutions as x_1 and x_2 which can exist in equilibrium with each other at a constant temperature are known as *conjugate solutions*.

The relative proportions of the two conjugate solutions corresponding with any mixture are readily obtained from the diagram. Thus a mixture of phenol and water represented by y at $t_1°$ C. will consist of layers of composition represented by x_1 and x_2 in

quantities proportional to the lengths BC and AB respectively.

The region enclosed by the curve is thus one of limited solubility. On increasing the temperature, the relative proportions of the two conjugates vary, and at $t_2°$ y consists of one saturated solution only; then if the temperature be increased still further, this solution becomes unsaturated. Above the temperature corresponding to the maximum in the solubility curve, the two liquids are soluble in all proportions.

On cooling, the changes occur in the reverse order. A mixture represented by z will consist of one unsaturated solution at temperatures above $t_3°$. At this temperature the liquid becomes saturated, and, on further cooling, breaks down to yield two conjugate solutions. At $t_2°$ there will be DF parts of the saturated solution y in contact with FE parts of the saturated solution z_1. The compositions of the two conjugate solutions will then vary along the two branches of the solubility curve as the temperature falls, until at $t_1°$ there will be AG parts of the solution x_2 in contact with CG parts of x_1.
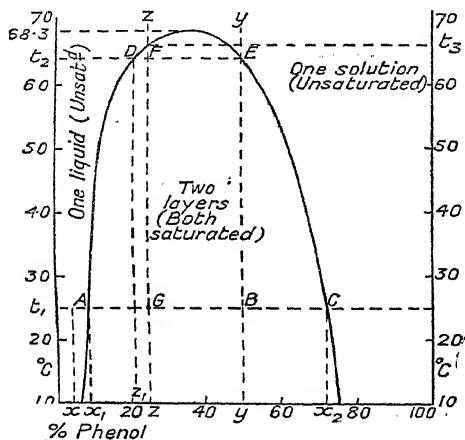
Fig. 45.—Solubility Curve for Phenol and Water

The same classification is applicable to solids as to liquids; thus solids may be completely soluble, partially soluble, or completely insoluble in each other.

In the case of complete insolubility in the solid state, the completely solid field is separated from all others by a horizontal line drawn from one extremity of the diagram to the other, just as in the case of aluminium and lead.

If the two solids are completely soluble in each other in all proportions, then the curve of solid solubility lies wholly within the solid range.

In the case of limited solubility, however, the solid solubility

curve is not complete, but, in a binary system, two branches only are obtained, since at some definite temperature the conjugate solid solutions then existing go direct to a homogeneous liquid (fig. 54, p. 78).

Cooling Curves of Pure Metals and Alloys.

When a pure metal is heated, the temperature steadily rises until the metal begins to melt, and then remains stationary until all the metal has become molten, after which the temperature again steadily rises. On cooling, the temperature falls regularly until the metal freezes, when a constant temperature is maintained until it is completely solid. The temperature of the solid metal then falls regularly, and if corresponding time and temperature observations are taken and the results plotted, a curve of the type shown in fig. 46 is obtained.

Fig. 46.—Cooling Curve of Pure Metal

The arrests or halts in the heating or cooling curves are a measure of the quantity of heat required to change the metal from the solid to the liquid state, and the quantity of heat required per unit mass of the substance is known as the *latent heat of fusion*.

The temperature at which liquefaction occurs is known as the *melting-point*, whilst that at which the liquid metal solidifies is called the *freezing-point*.

With perfectly pure metals, the freezing-point is the same as the melting-point. Alloys in general do not freeze at a constant temperature, but do so over considerable ranges of temperature, and the melting-point of an alloy is defined, therefore, as the temperature at which the alloy begins to melt, and in a similar manner the freezing-point denotes the commencement of solidification. The melting-point of an alloy is thus, in general, lower than its freezing-point.

Undercooling.

Many metals, when cooled from the liquid state, exhibit the phenomenon of undercooling, i.e. the liquid may be cooled to a temperature which is below the true freezing-point of the metal,
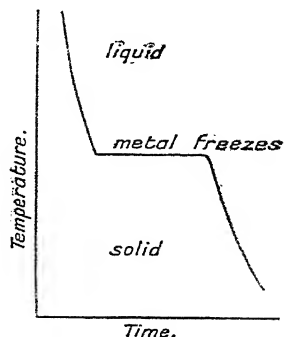
so that curves similar to that shown in fig. 47 are obtained when cooling data are plotted. As will be evident from an examination of the curve, there is a limit to the degree of undercooling, beyond which the metal crystallizes spontaneously, the temperature then rising to what is assumed to be the true freezing-point, denoted by the horizontal branch in the curve. There is, however, the possibility that this temperature may be slightly less than the real freezing-point, and undercooling is therefore undesirable when such metals are used for the calibration of pyrometers.
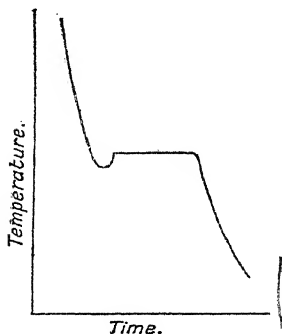
Crystal growth in a liquid is initiated by germs or nuclei, and the absence or insufficiency of these gives rise to undercooling. These germs in many cases are sub-microscopic, and their real nature has not yet been definitely established. Undercooling in liquids is inhibited by either stirring or inoculation with particles of the solid phase.

Undercooling occurs with liquid alloys and many solid solutions. In both these cases supersaturated solutions are obtained as a consequence. The undercooling of solid solutions is of extreme practical importance, since the hardening of steel and the " ageing " of duralumin and certain other alloys depend on this phenomenon.

The Diagram of Thermal Equilibrium—Eutectics.

It has already been mentioned that, in general, the addition of a small quantity of a substance to another in which it is soluble lowers the temperature at which the solvent commences to freeze. This lowering of the freezing-point increases with increasing proportions of the added solute.

Let it be assumed that two substances A and B, whose freezing-points are $t_1°$ and $t_2°$ respectively, are *completely soluble in the liquid state*. The gradual addition of B to A results in a progressive lowering of the freezing-point of the solution, the line t_1E (fig. 48), therefore, being the freezing-point curve for solutions of B in A; t_2E is similarly the freezing-point curve for solutions of A in B. These two lines are not necessarily straight, but in many cases are distinctly curved.

Time.

Fig. 47.—Cooling Curve of Metal showing Undercooling

It is obvious that the two lines will intersect in some point E, and a mixture of the two substances represented by C will therefore have the lowest initial freezing-point of the whole series. E is called a *eutectic point*, the composition C the *eutectic composition*, and the corresponding temperature ($t_4°$) the *eutectic temperature* (Greek εὔτηκτος = easily melting).

Now if the lines t_1E and t_2E are freezing-point curves, and any point on either branch indicates the temperature at which the corresponding alloy commences to freeze, then t_1E and t_2E may also be considered as solubility curves, since points on these lines represent saturated solution concentrations at definite temperatures. Above these lines, therefore, is a region in which the liquid substances are completely soluble in each other in all proportions, whereas, in regions below the curves, the substances are soluble to a partial or limited extent only.

Fig. 48.—Thermal Equilibrium Diagram—metals completely soluble in the liquid but insoluble in solid state.

Let it now be further assumed that the substances are *completely insoluble in the solid state*, and consider the cooling of a member of the system whose composition is represented by *x*. At temperatures above $t_3°$ the alloy consists of a homogeneous liquid solution, but at $t_3°$ the liquid becomes saturated and commences to freeze at this temperature. If the two substances are insoluble in the solid state, the deposited solid must be pure A, in view of the fact that the original liquid is richer in A than is required to yield the eutectic alone. Further, the deposition of pure A continues as the temperature falls. The remaining liquid thus becomes richer in B, and, since there is only one saturated liquid solution capable of existence at each temperature, the composition of the liquid gradually changes along the line t_1E, until finally it attains eutectic composition, and the residual liquid freezes at the constant temperature $t_4°$, the two constituents A and B, of the eutectic liquid, freezing out side by side.
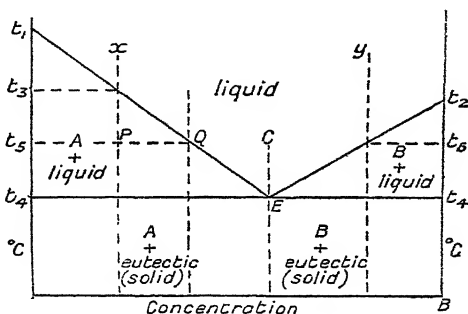
An alloy of composition C, therefore, will undergo no change in constitution whatever until the temperature $t_4°$ is reached, when the whole of the alloy freezes.

Similarly, a liquid of composition y commences to freeze at $t_6°$, but in this case the primarily deposited solid is pure B, the composition of the residual liquid then changing along t_2E until at $t_4°$ the remaining liquid freezes as a eutectic.

All the alloys of the series must therefore contain some proportion of eutectic when completely solid.

A diagram such as that described above, which indicates the constitution of any member of the system of the two metals at any temperature, is known as a *binary thermal equilibrium diagram.* Again considering the alloy whose composition is given by x, its constitution at a temperature $t_5°$ is given by PQ parts of pure A in contact with Pt_5 parts of liquid of composition Q_1.

The lines t_1E and t_2E, which separate the field of complete liquidity from all others, constitute what is known as the *liquidus,* and the line t_4Et_4, separating the field of complete solidity from any other, is called the *solidus.*

Binary systems yielding diagrams similar to that described are the water-salt, bismuth-tin, and lead-tin systems, in which well-defined eutectics are obtained. ·

The cooling curve of a true eutectic is of the same form as that of a pure metal.

The Structures of Pure Metals and Alloys.

Crystallization begins from a series of centres, and the small crystals first formed then grow, and, if free to develop, may exhibit some well-defined geometrical shape. Thus a hot saturated solution of potassium chloride in water, on cooling, deposits cubic crystals which grow in size as the temperature falls; and if no obstruction is encountered, the growth is the same in all directions.

Such crystals, which exhibit a definite external geometrical shape, are known as *idiomorphic crystals.*

In all pure metals and in many alloys the solid crystals grow from a series of centres in the cooling liquid, and although in the earlier stages these crystals may have idiomorphic shapes, they increase in size, impinge, and mutually limit growth. An etched section from such a solid is found to be covered by a network of lines, these indicating the impingement and forming the boundaries of *allotriomorphic crystals.* Although these have no apparent

geometrical form, their internal molecular symmetry is just as perfect as that of the idiomorphic crystals.

The small crystals initially formed show a decided tendency to grow in the direction of certain axes, which gives rise to elongated and branched forms known as *crystallites* or *crystal skeletons*. Thus there are several directions in which growth may take place to the greatest extent, and it has been shown that growth rapidly occurs at the sharp corners of the crystallites also. Once the solid skeleton is formed, therefore, a series of secondary axes are established at right angles to the primary axes, and these are succeeded by tertiary and higher orders, which ultimately results in the filling-up of the original skeleton. With salts growing in solution, this filling-up keeps pace with the axial growth, and hence the crystal is more or less uniform in all directions.

With metals, however, the axial growth is at a greater rate than the filling-up, and elongation of the crystals in the direction of certain axes occurs. Examples of this type are sometimes found in the heads of large steel ingots: the metal in the head is the last to freeze, and there is not sufficient material left to fill in the interstices.

With pure metals the crystal skeletons have the same composition as the infilling, and hence each crystal is perfectly homogeneous. As already indicated, therefore, microscopic examination merely reveals a series of irregularly shaped crystal grains, the grain boundaries constituting the impingement lines between neighbouring crystals.

If the solid matter which is deposited from the liquid is a solid solution, crystallization occurs in exactly the same manner, and if diffusion is complete, each individual crystal is quite homogeneous, the solid solution then having a similar appearance under the microscope as a pure metal (figs. 156, facing p. 216, and 168, facing p. 226).

The primary crystallites may shoot out into the liquid in almost any direction, and thus when a plane section of the solid metal is examined, the plane of section will cut the principal axes of different crystals at different angles. These crystals are not isotropic, i.e. their properties are not quite the same in all directions, and consequently when etched the crystals are attacked in varying degrees. When examined under the microscope, therefore, the grains exhibit different shades of colour owing to interference of light.

If the rate of cooling of an alloy which forms solid solutions is

not sufficiently slow to allow complete diffusion to occur, the original skeleton structure is more or less retained. Each crystal grain is then not homogeneous, and a difference in composition exists between different parts of the same crystal. After etching, the crystals then exhibit a tree-like appearance (figs. 25, 26, 155, 167). Such structures are known as *cored* or *dendritic crystals*.

Most cored structures can be obliterated by prolonged annealing, i.e. heating to such a temperature that equilibrium is restored and complete diffusion occurs, so that on subsequent examination under the microscope only the crystal boundaries are revealed.

Eutectic Structures.

Alloys of eutectic composition freeze at constant temperatures. The two constituents of a binary eutectic may be pure metals,
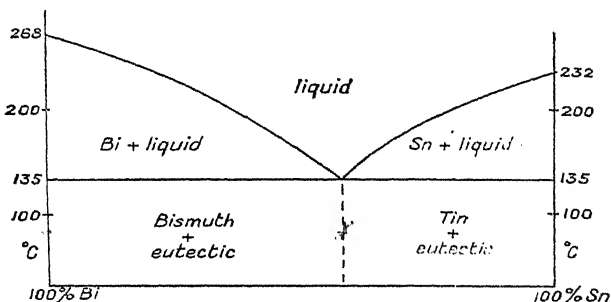

Fig. 51.—Bismuth-tin Equilibrium Diagram

solid solutions, or definite chemical compounds. When subjected to micro-examination, very beautiful patterns showing a somewhat laminated appearance are revealed, such as those shown in figs. 49 and 50.

Homogeneous solid solutions may break down in a similar manner, and then exhibit similar microstructures. In order to distinguish these structures from true eutectics, the term *eutectoid* is applied. The constituents of a eutectoid are also deposited side by side at constant temperature, but from a solid solution. Familiar eutectoid structures occur in the copper-aluminium alloys, the α—δ bronzes, and in steel.

The alternate light and dark shades in eutectics and eutectoids are simply due to the differential attack of the etching medium
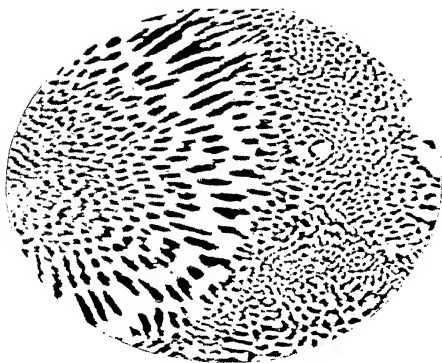
Fig. 49.—Silver-copper eutectic
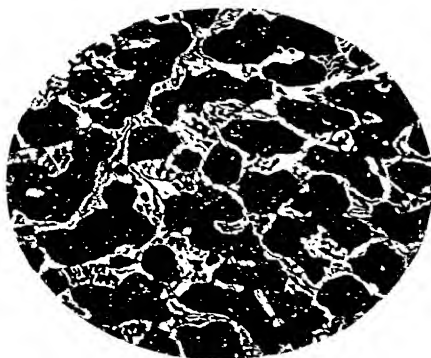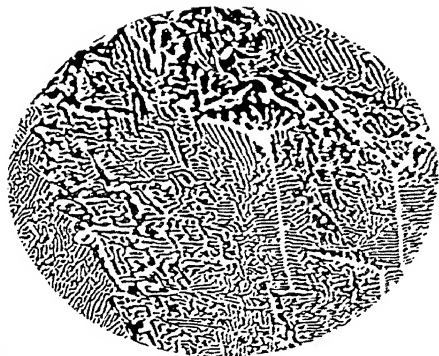alloy.   × 75

Fig. 50.—Bismuth-tin eutectic
alloy.   × 75

Fig. 52.—Bismuth-tin alloy: 20
per cent Bi, 80 per cent Sn.   Dark
areas are primary tin crystals and
composite areas are the eutectic.
× 75.

employed. The constituent which is attacked to the lesser extent stands up in relief and appears light in colour, but shadows are cast into those parts which are etched to the greater extent, hence these appear dark when examined under the microscope.

The microstructure of a member of a binary system may be predicted from a consideration of the equilibrium diagram.

The bismuth-tin diagram is given in fig. 51.

An alloy containing less than 40 per cent bismuth and more than 60 per cent tin will consist, when solid, of primary crystals of tin embedded in a eutectic background. As the composition approaches that of the eutectic, the relative amount of the primary tin crystals decreases, but as the composition proceeds beyond the eutectic, primary bismuth crystals appear, and are obtained in increasing proportions. A typical microstructure is shown in fig. 52.

Other Equilibrium Diagrams.

When the two metals are completely soluble in both liquid and solid states, the thermal equilibrium diagram is of the type repre-
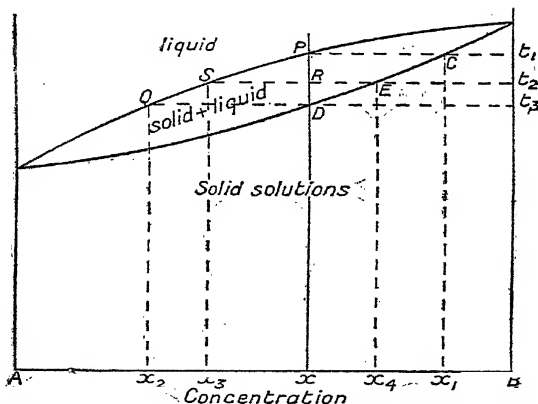

Fig. 53.—Thermal Equilibrium Diagram of Binary System in which complete solubility occurs in both liquid and solid states

sented in fig. 53, from which it is evident that the melting- and freezing-points lie between those of the pure metals.

Under these circumstances, the curve of solid solubility lies wholly below the solidus, and the solid alloys form a continuous

series of homogeneous solid solutions at all temperatures lying between the solidus and the maximum of the solid solubility curve. The liquidus is denoted by the upper and the solidus by the lower curves.

The process of freezing of any one alloy will serve to illustrate that of any other member of the system. Thus a liquid of composition x begins to freeze at $t_1°$, but since the metals are soluble in each other in the solid state, the crystals then deposited will have the composition x_1, since this is the only solid solution capable of existence 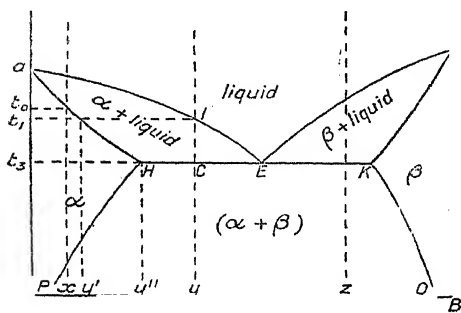in contact with the liquid at this temperature. As the temperature falls, more solid solution crystals are deposited, but these, together with those deposited at $t_1°$ and at any subsequent temperature, must necessarily change, by absorption of the liquid, to form solid solutions having compositions indicated by the points on CD corresponding to the temperature.

Fig. 54.—Equilibrium Diagram. The two metals are completely soluble in the liquid but only partially soluble in the solid state.

The crystals first deposited are richer in B than the original liquid, and the liquid remaining thus becomes richer in A. The constitution of the liquid during freezing then varies along the liquidus PQ. At $t_3°$ the alloy is completely solid and consists of homogeneous solid solution crystals of the same composition as the original liquid, the last theoretical drop of liquid having the composition x_2, whilst at some intermediate temperature $t_2°$ there will be RE parts of liquid of composition x_3 in contact with RS parts of solid solution crystals of composition x_4.

The copper-nickel alloys yield a diagram of the above type.

A diagram of considerable industrial importance is that of fig. 54, which represents a binary system in which the two metals are completely soluble in the liquid, but only partially soluble in the solid state. In this case, two branches only of a solid solubility curve are obtained which meet the solidus in, say, H and K, and a eutectic of two solid solutions is formed. An alloy of composition

x freezes in an analogous manner to that of any member of the preceding system, but although the alloy consists of a homogeneous solid solution at $t_4°$, it may break down into two conjugate solid solutions at lower temperatures if the vertical through x cuts the branch PH of the solid miscibility curve. y, on cooling, deposits primary crystals of composition y' at $t_1°$, which, together with those deposited as the temperature falls, change in composition by diffusion along aH, until at $t_3°$ they have the composition y''. The liquid meanwhile varies in constitution along IE until at $t_3°$ the residual liquid solidifies as a eutectic of the saturated solid solutions H and K.

Commencing at the left-hand side of these and more complex diagrams, the separate series of solid solutions are indicated by the Greek letters $α$, $β$, $γ$, &c.

When just solid, y will consist therefore of primary $α$ solid solution crystals embedded in a matrix of eutectic of $α$ and $β$, and in the relative proportions CE of $α$ to CH of eutectic. Below $t_3°$, both H and K break down into conjugate solid solutions. The structure of the solid alloy at $t_3°$ is, however, more or less retained.

z would deposit primary $β$ solid solution crystals, and when just solid, would consist of primary $β$ crystals of composition K in a eutectic background.

The properties (hardness, conductivity, &c.) of the $α$ solid solutions exhibit a gradual variation as the concentration increases. The $β$ alloys also show this gradual variation, although their general properties may differ from those of the $α$ alloys to a very marked extent.

Solid solutions are not generally homogeneous in the cast condition, but, as already mentioned, cored or dendritic crystals result, and this may influence the microstructure of the resulting alloy in other respects. Thus, in the system just considered, some of the $α$ solid solution alloys may contain considerable amounts of eutectic in the cast condition, and the properties of such alloys are then modified to quite an appreciable extent. Consider, as an example, the actual freezing of an alloy of composition x (fig. 55), which, under true equilibrium conditions, should consist entirely of $α$ solid solution crystals when solid. At $t_1°$ this alloy deposits crystals represented by x_1, and at $t_2°$ there should exist PM parts of solid solution crystals in contact with Px_2 parts of liquid. The rate of cooling, however, will not generally be sufficiently slow to allow complete diffusion to occur, whereby the original x_1 crystals

are transformed to the composition represented by x_2, and the liquid is then richer in B than it should be under equilibrium conditions. As a consequence, the proportion of liquid at $t_2°$ will be greater than Px_2, and the relative proportions of liquid and solid will be more nearly represented by Bx_2 and BM respectively. Similarly at $t_3°$, when the alloy should be completely solid, some liquid will still remain, the relative proportions of liquid and solid being given by Cx_3 and CN.

Even at $t_4°$ the alloy may not be completely solid, and the liquid remaining will have eutectic composition, and then freeze
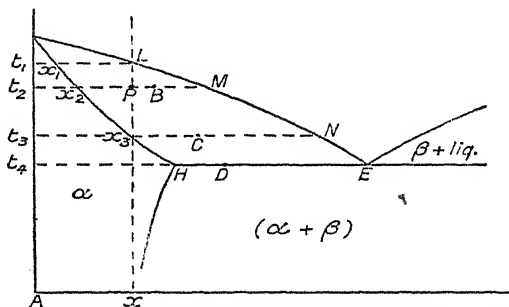
Fig. 55.—Illustrating the Freezing of an Alloy where the cooling is not at a sufficiently slow rate to allow complete diffusion to occur

as a eutectic at this constant temperature. The completely solid alloy will thus consist of cored $α$ solid solution crystals with some eutectic entrapped between them.

On annealing, the eutectic areas would disappear, the composition of each $α$ crystal would become that of x, and the coring would disappear.

Intermetallic Compounds.

It is sometimes found that the two metals involved in a binary system enter into definite chemical combination. Such a compound is a member of the system, and is termed an intermetallic compound. Familiar examples are Cu_3Sn, $CuAl_2$, Mg_2Si, Fe_2W; and there are many others.

The existence of an intermetallic compound in a series may be indicated by a maximum in the liquidus curve (fig. 56), and the compound may then be regarded as forming binary systems with each of the constituent metals. This will be evident from a con-

sideration of the figure shown, which is constructed on the assumption that the compound is completely insoluble in both of the constituent metals in the solid state.
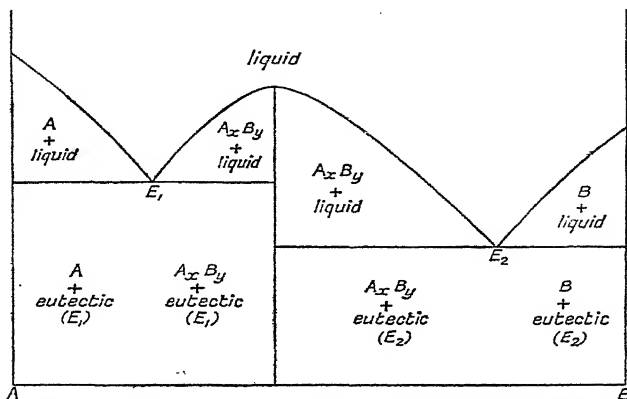
Fig. 56.—Thermal Equilibrium Diagram showing Occurrence of an Intermetallic Compound (A_xB_y)—compound and each metal completely soluble in the liquid but insoluble in the solid.

Similarly, in cases where the compound is partially or completely soluble in the solid, the complete diagram can be regarded as being built up of two of the simpler types already considered.

Peritectic Transformations.

In certain cases, during the freezing of an alloy, interaction occurs between solid matter already deposited and the residual liquid to form a new constituent. This interaction occurs at a constant temperature, and the alloy is then said to undergo a peritectic change. The constituent formed at the peritectic temperature may be an intermetallic compound, although more often it is a solid solution of a different concentration far removed from that primarily deposited.

Diagrams of this type are represented in figs. 57 and 58, and the freezing of several members of each system will be considered.

In fig. 57 any alloy with a composition intermediate between pure A and H will freeze in a similar manner to that of x in fig. 54.

An alloy y, lying between H and K, deposits a solid solution crystals throughout the range t_1–t_2, the a crystals varying in

composition along the branch of the solidus aH until at $t_2°$ they
have the composition corresponding to H.   The liquid meanwhile
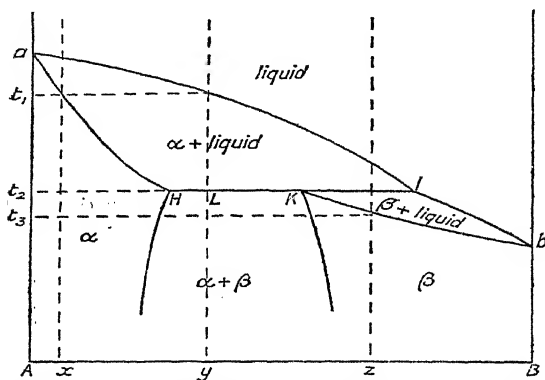
Fig. 57.—Binary System in which one Solid Solution is formed at a
Peritectic Temperature

changes its composition along the liquidus aI until at $t_2°$ it has the
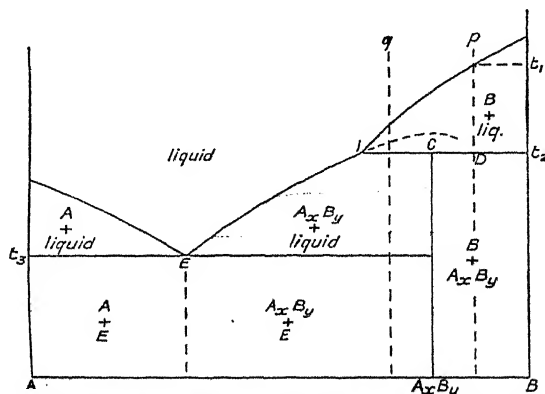composition corresponding to I.   When this temperature is reached

Fig. 58.—Binary System illustrating Compound at a Peritectic Temperature

there will exist LI parts of H crystals in contact with HL parts of
liquid I   At this temperature the a crystals interact with the

liquid to yield β solid solution crystals represented by K, but since the original liquid is not rich enough in B to yield all β solid solution crystals, some H crystals remain unchanged and the alloy becomes completely solid at $t_2°$.

The just solid alloy then consists of α solid solution crystals of composition H and β crystals of composition K in the relative proportions LK of α and HL of β. Both these conjugate solutions break down as the temperature falls, the general structure, however, remaining more or less the same.

Alloy z freezes in a similar manner, but since the composition is such that it contains more B than is required to form the solid solution K, all the primary α crystals are transformed, at the peritectic temperature by interaction with the liquid, into β crystals, and some liquid still remains. This remaining liquid subsequently deposits more β solid solution crystals throughout the range t_2–t_3, the composition of these β crystals, as well as those formed at the peritectic change, varying in constitution along the solidus branch Kb. At $t_3°$ the alloy will be completely solid, and consist of homogeneous β solid solution crystals of the same composition as the original liquid.

In fig. 58 p deposits crystals of pure B throughout the range t_1–t_2, and at the latter temperature there would be pure B crystals in contact with liquid I in the relative proportions ID of B and Dt_2 of liquid. Interaction then occurs to yield the intermetallic compound A_xB_y, but since the original composition is such that there is insufficient A to yield all A_xB_y, some of the primary B crystals remain unchanged, the solid alloy then consisting of pure B crystals and A_xB_y crystals in the proportions CD and Dt_2.

q freezes in a similar manner, but all the primary B crystals are transformed at the peritectic temperature to form A_xB_y, and some liquid I remains. This liquid then deposits more A_xB_y throughout the range of temperature t_2–t_3. The liquid thus varies in constitution along the liquidus branch IE, until at $t_3°$ it attains eutectic composition and freezes at constant temperature. q, therefore, when solid, consists of A_xB_y crystals together with some eutectic.

Alloys intermediate in composition between A and E freeze in a similar manner to those of fig. 48, and need not therefore be discussed here.

Many other types of thermal equilibrium diagrams are theoretically possible, but the industrial alloys generally yield combinations of the simple types already given.

Ternary Alloys.

Metallic systems consisting of three metals are known as ternary systems, and, just as in binary systems, solid solutions and eutectics are often obtained. Many ternary eutectics have extremely low freezing-points.

The composition of any member of a ternary system is indicated by a point within an equilateral triangle, and the third dimension is then used to indicate temperature. A ternary system is therefore only truly represented by a space model, although the liquidus and solidus surfaces can be indicated in a convenient fashion by projecting upon the equilateral base the isothermals drawn upon them.

Changes which occur during Cooling after Solidification is Complete.

The condition of an alloy just after solidification is not necessarily final and unalterable, since the material is susceptible to change by thermal and mechanical operations, which may exert an effect on the microstructure. The constituents of solid alloys may be pure metals, intermetallic compounds, or solid solutions; and internal changes in a metal or compound present in solid solution must exert some influence on the nature and properties of the solid solution.

Allotropy.

The fact that certain substances are capable of existing in more than one crystalline form is generally known. Familiar examples of allotropic elements are carbon, phosphorus, and sulphur. The various allotropic modifications are only stable within certain more or less well-defined limits of temperature and pressure, and the change from one form to the other is often accompanied by an alteration in other physical properties. Of the metallic elements, iron and tin are the best-known allotropic substances.

Iron crystallizes in the cubic system, and when free to grow the crystals are generally octahedra. The element exists in several forms which are given below:

α iron—stable below 760° C.;
β iron—stable between 760° and 900° C.;
γ iron—stable between 900° and 1405° C.;
δ iron—stable between 1405° and the melting-point 1535° C

The exact arrangement of the atoms in the unit cubes of iron in its various modifications has been determined only within the last few years. X-ray examination has shown that γ iron is built up of " face-centred " cubes, each cube containing an atom at each corner and an atom at the centre of each of the six faces (fig. 59). Thus, since each corner atom, of which there are 8, is common to 8 cubes, and each " facial " atom (6 in number) is common to two cubes, there are in effect $\frac{8}{8} + \frac{6}{2} = 4$ atoms per cube.

a, β, and δ irons consist of a " body-centred " lattice in which there is one atom at each corner and one at the centre of each cube (fig. 60), i.e. in effect $\frac{8}{8} + 1 = 2$ atoms per cube. Thus it might
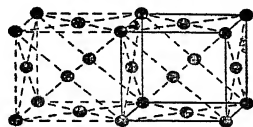
Fig. 59.—" Face-centred " Lattice of γ Iron
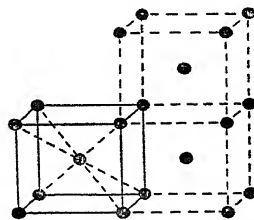
Fig. 60.—" Body-centred " Cubic Lattice of a and δ Iron

be expected that the closer packing of the atoms in the γ modification immediately on its production would result in a contraction. This change is, however, accompanied by an alteration in the length of each cube edge. These lengths have been determined, and at 900° C. are given as 2·89 and 3·64 Ångström units for a iron and γ iron respectively. Thus, although an actual volume change does occur, its magnitude is not nearly so marked as the above data would suggest. The dilatation curve for pure iron is given in fig. 61 (due to Satô) *, from which it will be observed that the coefficient of either a or δ iron differs considerably from that of the γ modification, and these volume changes are of importance in connexion with the heat-treatment of steel. It will also be noticed that the expansion curve for δ iron is continuous with that for a iron, thus giving further evidence that these two modifications are in reality one and the same. The a–β change is accompanied by a very

* *Imperial Science Reports*, Tokio

pronounced alteration in the magnetic properties of the iron, provided that only small magnetizing forces are employed, as will be evident from fig. 62, where a magnetizing force of 0·5 Gilberts was used. With stronger fields, the maximum in the curve becomes much less pronounced and occurs at lower temperatures,
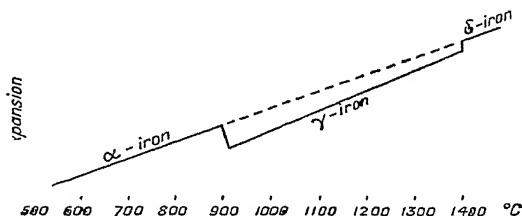
Fig. 61.—Expansion-temperature Curve for Pure Iron

until with a magnetizing force of about 10 Gilberts the curve is almost flat, and the permeability falls steadily at temperatures beyond about 150° C. X-ray examination shows that the α–β change is not accompanied by any alteration in the space-lattice, and it is not regarded therefore as a true allotropic transformation.
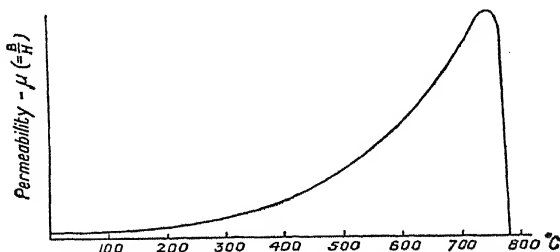
Fig. 62.—Variation of Permeability with Temperature for Pure Iron and small Magnetizing Forces

Tin is capable of existing in at least three forms. Grey or α tin is a form stable only below 19° C., whilst rhombic or γ tin exists above 160° C. Between 19° C. and 160° C. the stable form is β or tetragonal tin. This is the ordinary form which is met with, and consequently is really in an unstable condition. In the colder parts of the world β tin gradually changes to the α form, a change which is accompanied by the complete disintegration of the metal into a

fine grey powder. In such parts particles of α dust may be carried by the winds, and, if these are deposited on other tin articles they act as inoculants for the more rapid breakdown of such articles into powder form. Under such circumstances, the attacked articles have every appearance of being smitten by a disease, and on this account the term " tin pest " has been applied to this most peculiar phenomenon. Allotropic changes are often accompanied by marked evolutions or absorptions of heat, and this effect is shown in the heating and cooling curves of the pure metals. The allotropic transformations persist in the alloys of the metals when the
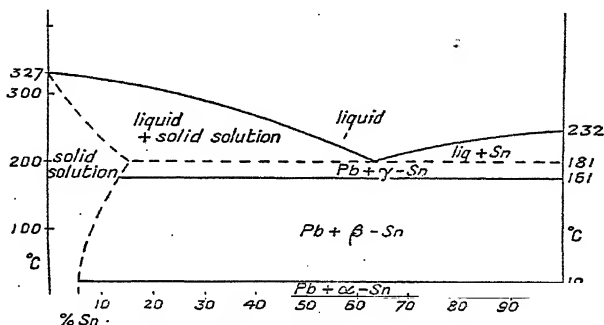
Fig. 63.—Equilibrium Diagram for Lead-tin Alloys

proportion of the added material does not exceed a certain limit, although the temperature of the change may vary considerably, but uniformly. This is evident from the consideration of the iron-iron-carbide diagram (fig. 72, p. 93) and the lead-tin diagram (fig. 63). The introduction of a third constituent may also result in the complete suppression of certain allotropic changes. In the silicon-iron alloys the α–γ change is completely suppressed if the silicon content exceeds a certain value (fig. 110, p. 141), and many alloying elements, of which the most important is carbon, completely eliminate the α–β change.

Recrystallization from Solid Solutions.

As already indicated, there exists a very close analogy between the freezing of liquid solutions and the breakdown of some solid solutions. Secondary crystallization may therefore occur in com-

pletely solid alloys, yielding analogues with crystal skeletons, eutectoids, &c. Two particular cases arise, and will be considered.

(a) A homogeneous solid solution breaks down into secondary crystals and a eutectoid, the constituents of the eutectoid being pure metals, compounds, or solid solutions. Such eutectoids occur in the iron-iron-carbide and the copper-aluminium systems.

(b) One homogeneous solid solution breaks down into two conjugate solid solutions without the formation of a eutectoid, such as in the copper-zinc and the copper-tin alloys.

In either case, owing to the rigidity of the material and its increased internal viscosity, ordinary rates of cooling do not permit a separating component to assume the familiar shapes of primary crystals formed from liquid solutions; and this affords a means of distinguishing between primary and secondary crystallization in many cases. Crystallization may commence at the grain boundaries of the original solid solution, but proceeds inwards along the cleavage planes of the crystals. Most metals crystallize in the cubic system, and the matter deposited from their solid solutions is put down along planes parallel to the faces of the cube or the octahedron, thus giving rise to the ultimate formation of a " latticed " pattern known as a *Widmanstätten structure* (figs. 77, facing p. 98, and 161, facing p. 220). When the amount of deposited matter is relatively small, a cellular structure is obtained, and structures of the Widmanstätten type are only produced if sufficient matter is deposited from solution to make the growth along the cleavage planes more or less complete. Thus in the case of steel castings containing up to 0·6 per cent of carbon, the structures are of this type, but between 0·6 and 1·3 per cent of carbon cellular structures are obtained. Outside these carbon limits, Widmanstätten structures prevail. The two types of structure are not altogether inseparable, and a combination of the two may be found in the same specimen. Both Widmanstätten and coarsely cellular structures are unsatisfactory from several points of view, and usually some further treatment, either thermal or mechanical, is necessary to modify them.

The Metallography, Heat-treatment, and Properties of Iron and Steel

Preparation of Ferrous Specimens for Micro-examination

A considerable amount of technique is involved in the preparation of micro-sections if the best results are to be obtained. Specimens are generally cut by means of a hack-saw, and a roughly prepared flat surface is then given to the specimen by a smooth file. The specimen should be rubbed along the file, otherwise a distinct convexity of surface is produced, so that when the specimen is examined under the microscope the whole of the field cannot be satisfactorily focused. Very hard materials may be ground flat on the side of a smooth emery wheel or grindstone. The file or wheel marks are then removed by rubbing the specimen on coarse emery cloth placed upon a smooth sheet of thick glass. The scratches put in by the cloth are afterwards removed by rubbing on still finer grades of emery paper. These papers are readily procurable, and the following series gives very satisfactory results: FF, O, OO, and OOO. To determine when the series of scratches caused by each grade of emery have been removed, it is an advantage to rub the specimen in such a manner that each new series is at right angles to those made by the previous paper. The fine scratches produced by the last emery paper are then obliterated by polishing the specimen on a revolving block covered with "Selvyt" cloth, which has been moistened with water and impregnated with some abrasive such as jewellers' rouge, or some form of finely powdered alumina, such as those sold under the trade names "Abradum" and "Diamantine".

When perfectly polished, the surface is entirely free from scratches and has a mirror-like appearance. With a few exceptions, the metal generally shows no structure when examined under the microscope. This absence of structure has been explained by the hypothesis that during polishing a non-crystalline or "amor-

phous " surface film is produced, flow having taken place to yield
an evenly distributed surface layer. In order to reveal the internal
structure of the metal, this surface film is dissolved by a suitable
etching reagent, whence the etching medium attacks the micro-
constituents in varying degrees.   In the cases of pure metals
and solid solutions, certain crystals, owing to their orientation,
become electro-positive to others, and a differential attack is main-
tained. In such cases, the crystal grains may vary in tint, although
all have the same chemical composition.   The etching media
generally employed for irons and steels are 2 per cent nitric acid
in alcohol or a saturated solution of picric acid in alcohol.   A
solution of sodium picrate containing excess of the alkali, in which
the specimen is boiled for about 30 minutes, is also useful as a
means for distinguishing between cementite and ferrite.   After
the final polishing, a much cleaner surface is obtained by lightly
rubbing with soapy water. This is applied with the finger and is
easily washed off under the tap; a uniform etching effect is then
obtained.   After etching, the specimens are thoroughly washed
under the tap in order to remove the slightest trace of the etching
medium and thus avoid any staining of the surface.   Finally, the
specimens are dried with alcohol. In sections containing graphite,
a much cleaner etched surface is obtained, and the graphite and
other constituents are more clearly defined, if the specimens are
washed entirely with alcohol, particularly when picric acid is used
as the etching medium.

Properties of Iron.

After polishing and etching, pure iron, when examined under
the microscope, is seen to consist of a series of polygonal crystal
grains (fig. 64). This substance is known as *ferrite*. Many alloying
elements (Cr, Ni, Si, Mn, &c.) are soluble in solid a iron.   The
solid solutions thus formed show similar microstructures, and the
term ferrite embraces any such solid solutions in which iron is
acting as the solvent.

Pure iron is a malleable metal, and has a Brinell hardness
number of about 96, with a tensile strength of about 20 tons per
square inch.

The Influence of Carbon on Iron.

Alloys of iron and carbon containing less than 0·89 per cent of
carbon, slowly cooled from a high temperature, and when examined

Fig. 66.—Pearlite in steel. Laths of cementite in ferrite matrix. × 500

Fig. 65.—Steel containing 0·08 per cent C. × 100. Pearlite (black) in ferrite (white background)

Fig. 64.—Showing ferrite crystals in pure iron

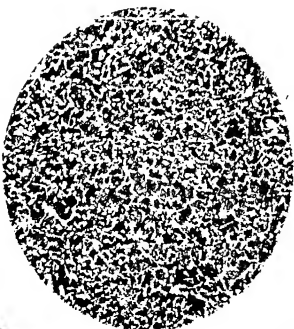Fig. 67.—Steel containing 0·21 per cent carbon. × 100

Fig. 69.—Steel containing 0·85 per cent carbon. × 100

Fig. 68.—Steel containing 0·49 per cent carbon. × 100

Fig. 70.—Steel containing 1·41 per cent carbon steel. × 100

under a low-power microscope, show areas of a dark-etching constituent in addition to the white ferrite (fig. 65). Higher magnifications resolve such darker areas into two constituents (fig. 66), the structure then resembling that of a eutectic. The new constituent is, in fact, a eutectoid, and consists of alternate lamellæ of iron (ferrite) and carbide of iron (Fe_3C). This eutectoid is known as *pearlite*, since many specimens, after etching, exhibit a play of colours resembling mother-of-pearl when seen at low magnifications. As the carbon content increases, the proportion of pearlite in the slowly cooled steels gradually increases, with a corresponding decrease in the amount of free ferrite, until 0·89 per cent is reached. A steel of this composition is apparently homogeneous at very low magnifications and consists entirely of pearlite, hence pearlite itself contains 0·89 per cent of carbon or 13·35 per cent of carbide of iron. Steels containing less than this amount of carbon consist therefore, when slowly cooled, of almost carbonless iron together with areas containing 0·89 per cent of carbon. When the total content of the steel exceeds this value, a new micro-constituent makes its appearance. This is free carbide of iron known metallographically as *cementite*. If nitric or picric acid is employed for the etching, the cementite appears more brilliantly white than does the ferrite. Sometimes, however, it is somewhat difficult to distinguish between the two constituents, but a boiling solution of alkaline sodium picrate, already referred to, affords a ready means of identification. Cementite then appears coloured, the ferrite remaining unaffected. As the carbon content of steel increases beyond 0·89 per cent the structurally free cementite increases in quantity. Cementite is not necessarily pure carbide of iron, and in steels containing elements other than carbon and iron additional carbides are formed which enter into solid solution with the iron carbide without alteration of the microscopical aspect. The term cementite is therefore applied to any such solutions of carbide. The fact that cementite is also a constituent of pearlite itself must not be overlooked, and to simplify the nomenclature somewhat, the carbide in the pearlite is often described as eutectoid cementite, whilst that which is structurally free is known as hyper-eutectoid cementite. The influence of carbon on the microstructure of steel is illustrated by figs. 67, 68, 69, and 70, whilst the diagram (fig. 71) represents the relative proportions of the above constituents present in the slowly cooled (annealed) steels. The tensile strength of pearlite in annealed

steels is about 37 tons per square inch, and an approximate value for the tensile strengths of steels containing less than 0·89 per cent carbon may be computed with the aid of this diagram. Thus a steel containing 0·5 per cent carbon will consist, in the annealed state, of about 45 per cent ferrite and 55 per cent pearlite, and from the values already given, this gives an average tensile strength of about 30 tons per square inch.

The relative proportions of ferrite and pearlite in the micro-structure may sometimes be taken as an indication of the carbon
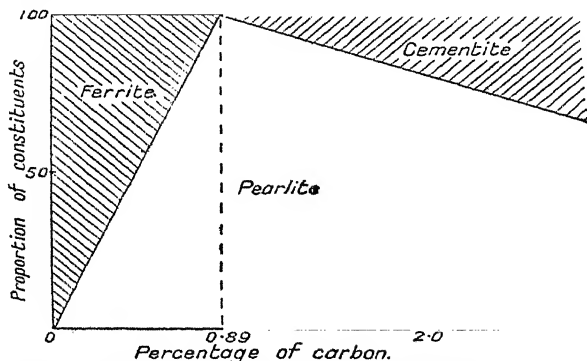
Fig. 71.—Illustrating Relative Proportions of Constituents in Slowly Cooled (Annealed) Carbon Steels

content of the steel, but as will be seen later, these proportions are influenced to a marked extent by the presence of other elements in the steel.

Cementite is an extremely hard, brittle constituent, with a Vickers diamond hardness number of about 600. Free cementite increases the hardness of steel, but this is accompanied by a drastic falling-off in the ductility values.

The Iron-iron-carbide Equilibrium Diagram.

The complete diagram is given in fig. 72, from which it will be observed that the addition of carbon to iron results in a lowering of the freezing-point from 1535° to 1130° C. Cementite is soluble in γ iron to the extent of about 1·8 per cent at 1130° C., but the solubility decreases with lowering temperature as indicated by the branch CD of the solid solubility curve. This curve intersects the

line AC in the eutectoid point C, at which the γ solid solution
changes to pearlite. At temperatures above these lines solid solu-
tions of carbide of iron exist, and any γ solid solution is known as
austenite. Austenite, therefore, may have any carbon content up
to 1·8 per cent. There is a peritectic transformation at 1490° C.,
at which δ iron solid solution is transformed to austenite; and
since the rate of cooling is generally such that this transformation
is incomplete, this has some influence on the structure of mild
steel ingots.

The two branches of the liquidus intersect in a eutectic point
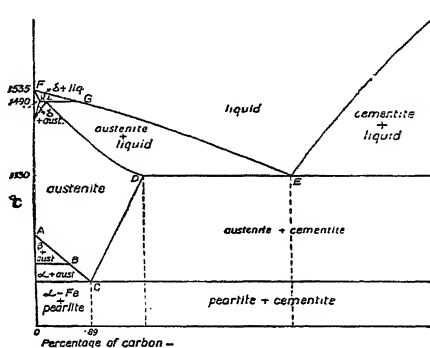
Fig. 72.—Equilibrium Diagram: Iron-carbon Alloys

corresponding with about 4·3 per cent carbon, the eutectic con-
sisting of cementite and austenite containing 1·8 per cent carbon.
Up to 1·8 per cent carbon the iron-carbon alloys are known as
steels, whilst those containing a greater proportion of carbon and
which should normally contain some eutectic are known as *cast
irons*.

Consider the freezing of an iron containing about 3·5 per
cent carbon. The primarily deposited matter is austenite. More
austenite is precipitated as the temperature falls, the composition
of the solid solution at each successive temperature being repre-
sented by points on the solidus LD, until at 1130° C. the austenite
should have a composition corresponding with D, i.e. 1·8 per
cent carbon. In the meantime the liquid decreases in bulk and
changes in constitution along the liquidus FE, until at 1130° C. it
attains eutectic composition and freezes at this temperature as a

eutectic of austenite and cementite. The structure then consists of primary austenite crystals embedded in the eutectic. As the temperature falls, however, the primary austenite crystals deposit cementite, the remaining solid solution then changing along DC until 695° C. is reached. At this temperature, the residual austenite contains 0·89 per cent carbon and changes to pearlite. The pearlite areas are thus enveloped by cementite which has been deposited during cooling. The austenite of the eutectic breaks down in a similar manner, which results in a thickening up of the cementite lamellæ in the eutectic at the expense of the austenite,
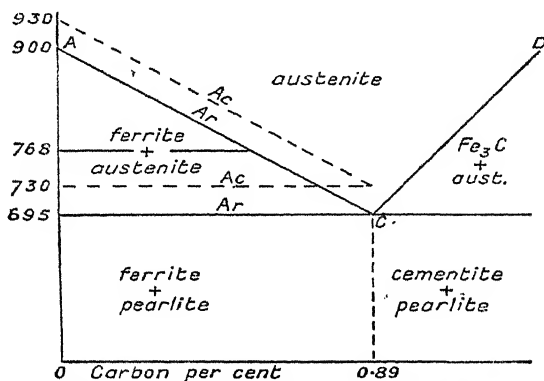
Fig. 74.—Heat-treatment Panel of "Steel" Diagram

which eventually reverts to pearlite. Such a structure is shown in fig. 73 (facing p. 98), in which the tree-like or dendritic appearance is readily observed. The structure shown in the figure is typical of the white irons which are subsequently subjected to a malleablizing treatment for the production of malleable iron castings (p. 20).

The most important part of the above diagram is that which is reproduced in fig. 74, and a complete interpretation of the significance of the lines thus drawn is essential for a knowledge of the principles upon which the heat-treatment of steel is based. Cooling curves of pure iron show two halts or arrests, one at 900° C. which denotes the change from γ to β iron, and the other at 768° C. representing the β–α change. These arrests are not sharply defined on most time-temperature curves, and it is more usual to plot the inverse-rate-temperature curves. These show

distinct " peaks " which correspond with the horizontal branches on the time-temperature curves. The inverse-rate curve for pure iron is given in fig. 75. The introduction of carbon results in a lowering of the γ–β change up to about 0·55 per cent of carbon, when this transformation no longer occurs; the γ iron then changing directly to the α modification. The introduction of carbon also gives rise to the occurrence of another peak in the cooling curve, at 695° C. The amplitude of this change (using specimens of the same mass) increases with increasing carbon content until 0·89 per cent is reached, when this is the only change which occurs, and hence this lower temperature transformation is associated with the formation of pearlite from the austenite or γ solid solution. The inverse-rate curves for several steels are given in fig. 76. If now the heating curve of any steel is plotted, the changes take place in the reverse order but at somewhat different temperatures. The pearlite - austenite change is found to occur at 730° C., i.e. there is a thermal " lag " or thermal hysteresis associated with this transformation amounting to about 35° C. The α–β change differs very little from that obtained on cooling, but the β–γ changes also

Fig. 75.—Inverse-rate Cooling Curve for Pure Iron

occur at temperatures 25° to 30° C. above the corresponding changes on cooling. This lag is important in connexion with the heat-treatment of steel, since the lower part of the equilibrium diagram, to which all heat-treatment temperatures are generally referred, has been determined from the data obtained on cooling. The temperatures corresponding with the arrests are known as *critical points* or " A " points; and in order to distinguish those obtained during heating and cooling, the initial letters of the French words chauffage (heating) and refroidissement (cooling) are used. Numbers are also used to represent the particular changes which occur, commencing from that which occurs at the lowest temperature. Thus in the case of a 0·2 per cent carbon steel, the following critical points are obtained:

On heating: Ac_1, 730° C.   On cooling: Ar_3, 860° C.
$\qquad\qquad\quad$ Ac_2, 770° C. $\qquad\qquad\qquad$ Ar_2, 768° C.
$\qquad\qquad\quad$ Ac_3, 885° C. $\qquad\qquad\qquad$ Ar_1, 695° C.

When two points merge into one, two numbers are used to denote the change-point. Thus in the case of a steel containing between 0·55 and 0·89 per cent of carbon, two critical points are obtained, the Ac_1 and Ac_{2-3} points on heating, and the Ar_{3-2} and Ar_1 points on cooling. Similarly, in the case of a 0·89 per cent carbon steel,
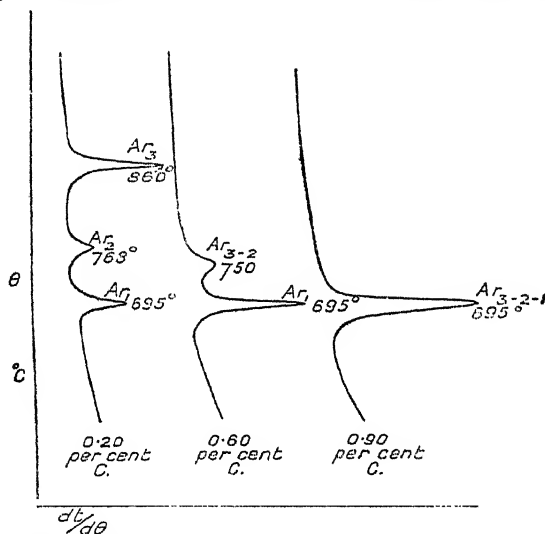
Fig. 76.—Inverse-rate Cooling Curves for Pure Iron-carbon Steels

the Ac_{1-2-3} and the Ar_{3-2-1} points are obtained. The critical points which are obtained on cooling are sometimes known as " recalescence ", and those on heating as " decalescence " points. The Ac points for steels containing up to 0·89 per cent carbon are denoted by the dotted lines in fig. 74, p. 94.

On heating, the constitution of a 0·89 per cent carbon steel does not change until the Ac_{1-2-3} point is reached. At this temperature, the ferrite and cementite of the pearlite mutually dissolve to give the solid solution austenite, the temperature remaining constant until this change is complete. The iron in the steel is now in the γ, whereas before it was in the α condition. This is

the reverse of the change on cooling at the Ar_{3-2-1} point.   A similar change occurs in the pearlite in steel containing less than 0·89 per cent carbon, but the free ferrite still remains in the α form at 730° C.   If the heating is continued, however, this ferrite is progressively taken into solution by the austenite and simultaneously changed to γ iron.   The carbon concentration of the austenite thus gradually decreases with increasing temperature until the upper critical point is reached, when the steel is perfectly homogeneous and consists entirely of austenite.   On cooling, changes occur in the reverse order.   Thus a 0·2 per cent carbon steel consists entirely of austenite of this carbon concentration above 860° C.   At this temperature, however, the austenite commences to deposit ferrite, and this precipitation continues throughout the range 860° to 695° C., the austenite meanwhile changing its constitution along the line AC (fig. 74, p. 94) until at 695° C. it has eutectoid composition and changes, at constant temperature, to pearlite.   The line AC, which indicates the upper critical points of steels containing less than 0·89 per cent of carbon, and which therefore indicates also the commencement of the precipitation of ferrite from austenite, is known as the *ferrite line*. Similarly the line CD, which denotes the primary deposition of cementite from austenite, is known as the *cementite line*.   Steels containing more than 0·89 per cent carbon are dealt with in the later section on tool steels.

Influence of other Elements usually present in Steel.

In addition to carbon, all commercial steels contain some proportions of silicon, manganese, sulphur, and phosphorus, and these elements have some effect on the properties of the steel.

Manganese is an essential constituent of most steels in view of its effect in promoting soundness and freedom from blow-holes. In tool steels, the proportion of the element does not generally exceed 0·5 per cent, since larger amounts may cause the material to crack during hardening, particularly when water is the quenching medium employed.   Manganese up to 1 per cent is present in many structural steels, and improves the tensile strengths of such materials without seriously affecting the ductility.   The amount of manganese in a structural steel of given carbon content and free from special elements is somewhat dependent on the mode of manufacture.   Thus, acid open-hearth steels generally contain about 0·5/0·7 per cent Mn, English Bessemer about 1 per cent,

whilst Swedish Bessemer and electric furnace steels generally contain 0·35/0·45 per cent of the element. The effect of manganese on iron is illustrated by the following figures, due to Arnold:

C.	Mn.	Y.P.	M.S.	Elongation.	Reduction.	Bend.
0·04	·02	14	22	47	76	180°
0·10	1·29	23	32	35	65	180°

The influence of manganese on the sulphur in steel will be considered later. Most of the manganese in steel is in solid solution in the ferrite, to which it imparts greater strength. The element also combines with some of the carbon to form manganese carbide (Mn_3C), which enters into solid solution with carbide of iron as a constituent of pearlite, and this influences the composition of the eutectoid. Steels containing manganese show more pearlite than pure iron-carbon steels of the same carbon content. Thus a steel containing 0·75 per cent carbon and about 0·8/0·9 per cent manganese is wholly pearlitic. In addition, the pearlite is much finer, even in the slowly cooled steels, and often shows a characteristic structure.

Silicon is almost invariably present in small amounts (up to 0·25 per cent) in steel, and even such small quantities exert a beneficial effect owing to the excellent deoxidizing properties of the element. Steel castings usually contain 0·25/0·3 per cent silicon, and this brings about a considerable modification of the Widmanstätten structure associated with the cast condition (figs. 77 and 78). In tool steels, the silicon is generally below 0·2 per cent, since higher percentages, in combination with somewhat low manganese content, tend to produce graphite precipitation during working and annealing.

Sulphur and Phosphorus.—These elements are unavoidable impurities in commercial steels, and are generally regarded as injurious. In tool steels, each element is kept below 0·035 per cent, otherwise the material tends to split when forged. The following figures, due to Arnold, show the effects of these elements on the mechanical properties of iron:

C.	S.	P.	Y.P.	M.S.	Elongation.	Reduction.	Bend.
04	·02	·02	14	22	47	76	180°
07	·02	1·36	29	29	0	0	0°
08	·97	·02	2·5	2·5	0	0	0°

The quantities of sulphur and phosphorus are exceptional, and far greater than is ever met with in practice; but the tests

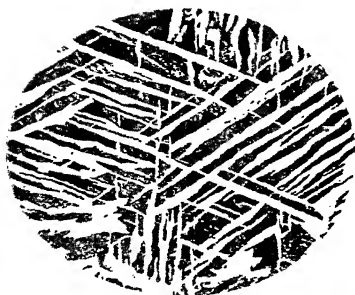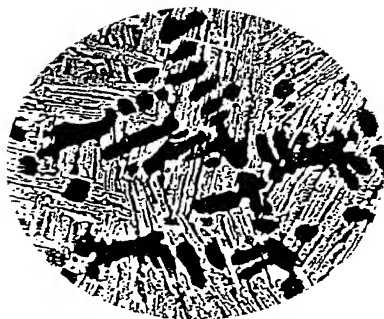Fig. 73.—White cast iron. Cementite (white) and pearlite (dark). × 100

Fig. 77.—Steel casting containing about 0·5 per cent carbon and very little silicon. Typical Widmanstätten structure. × 75.

Fig. 78.—Casting of similar composition, but containing about 0·5 per cent silicon. × 75.

Fig. 79.—Longitudinal section of a high sulphur steel showing streaks of manganese sulphide. Unetched. × 100.

certainly show the disastrous effect of phosphorus on the ductility of iron, and, in the case of sulphur, on both the tenacity and ductility. It will be noticed that the tenacity is considerably increased by phosphorus. In many structural steels 0·06 per cent of each element is permissible. Both elements are extremely liable to segregation, however, and therein lies the danger, since steels with an average sulphur and phosphorus content below 0·05 per cent have been known to show segregates containing more than 0·1 per cent of each.

Sulphur may exist in two forms in steel. In the absence of manganese, ferrous sulphide (FeS) is formed. This is a weak brittle constituent which forms intercrystalline films in the ferrite of low and medium carbon steels, and this accounts for the extremely poor tenacity value given above. Sulphur renders the steel both " hot " and " cold-short ", i.e. it cannot be forged either hot or cold. Ferrous sulphide appears as a yellowish brown constituent under the microscope.

In the presence of sufficient manganese, manganese sulphide (MnS) is formed instead of ferrous sulphide. Manganese sulphide is readily detected as a dove-grey constituent when the unetched specimens are examined (fig. 79). Unlike ferrous sulphide, manganese sulphide is plastic at high temperatures, and is therefore elongated into threads during forging and rolling. The material thus behaves in much the same fashion as slag in wrought iron, and has the similar effect of inducing a fibrous structure in steel. In order to ensure that all the sulphur in the steel is present as manganese sulphide, an excess of manganese to the extent of about four or five times that theoretically required is necessary. Provided that it is not present in too great a proportion, say below 0·05 per cent, manganese sulphide does not seriously impair the properties of most structural steels. The manganese content and the distribution of the manganese sulphide particles should always be considered before a steel is rejected on account of a sulphur content being slightly above specification limits.

Some estimate of the sulphur content of a steel can be obtained from the amount of manganese sulphide in the microstructure, but little indication of the manganese is so given, since most of the element is in solid solution in the iron.

Phosphorus in steel is generally too low to give rise to the production of the phosphide constituent referred to in connexion with cast irons, although it has been found in the piped portions

of some badly segregated steels. The element almost invariably exists in solid solution in the ferrite, thus accounting for the effect on the tensile strength of iron, and little indication of the phosphorus content is given by the microstructure. High phosphorus steels, however, often show a banded structure after rolling, ferrite streaks lying between bands containing the pearlite. Every endeavour is generally made during manufacture to keep the sulphur and phosphorus contents as low as possible, although lower percentages than ·012 per cent are not really desirable. Structural steels containing 0·02 per cent of each element have been found to be much more amenable to heat-treatment than those containing traces only; and so long as the distribution is uniform, better mechanical tests are obtained from specimens so treated. The only steels in which sulphur and phosphorus are intentionally high are the " free-cutting " steels used for the manufacture of nuts and bolts, &c. In such steels, each element may be as high as 0·15 per cent.

It is evident that serious consideration must be given to the chemical composition of a steel before a definite decision can be pronounced as to its suitability or otherwise for any specific purpose.

The mechanical tests of some commercial steels are given in the following tables:

ACID OPEN-HEARTH STEELS

Tests on the " as rolled " bars:

C.	Si.	Mn.	Y.P.	M.S.	Elongation.	Reduction of Area.
0·17	0·05	0·25	16	20	40	70
0·25	0·06	0·63	20	30	30	60
0·36	0·04	0·58	25	35	28	47
0·47	0·08	0·70	29	42	26	42
0·64	0·05	0·60	30	50	22	40
1·15	0·02	0·32	38	56	7	6
1·56	0·03	0·18	36	48	2	2

ELECTRIC FURNACE STEELS

Tests on normalized bars:

C.	Si.	Mn.	S.	P.	Y.P.	M.S.	Elongation.	Reduction of Area.
0·30	0·20	0·58	0·020	0·024	24	35	34	60
0·44	0·18	0·45	0·016	0·019	28	40	25	54
0·63	0·25	0·44	0·015	0·012	30	49	24	44

The Annealing of Steel.

Annealing consists in heating the steel to a high temperature, keeping it at this temperature for a specified time, and then slowly cooling it in the furnace.

Slow cooling generally results in the formation of pearlite showing a distinctly laminated appearance even at comparatively low magnifications, but although laminated pearlite is usually associated with annealed steel, its formation is also influenced by other elements which may be present in the steel. Thus, pure iron-carbon steels, and those containing much silicon, often show a
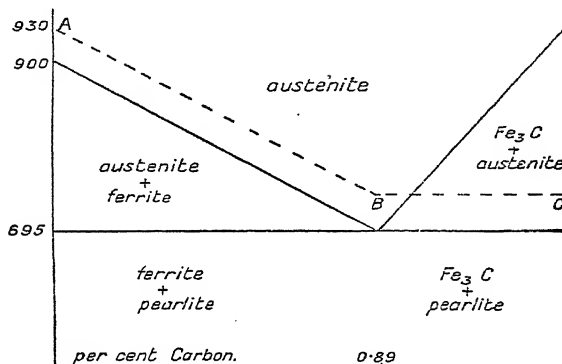
Fig. 80.—Annealing Diagram for Carbon Steels

coarsely laminated structure when the rate of cooling is only moderately slow, whilst high manganese steels may show a complete absence of lamination at magnifications below 500, even when very slowly cooled. For a given steel, however, the grade of the pearlite is certainly influenced by the rate of cooling, and the slower the cooling the grosser and more clearly marked are the laminations.

For steels containing less than 0·89 per cent of carbon the annealing temperatures are between 30° and 50° C. above the upper critical points, as indicated by the iron-iron-carbide diagram. These temperatures allow for the thermal lag associated with the critical changes, and also allow for very slight variations in the composition of the steel. Annealing temperatures for these steels

are therefore represented by the dotted line AB in fig. 80, and thus each steel is heated to such a temperature that it consists entirely of austenite. With steels containing more than this amount of carbon the conditions are somewhat different, and for these higher carbon steels the annealing temperature is denoted by the line BC, which is about 50° C. above the austenite-pearlite change-point. The reasons for this difference in the case of high carbon steels will be discussed in the later section on tool steels.

The dotted lines in the above diagram not only indicate annealing temperatures, but also constitute a general heat-treatment diagram for all steels free from special elements.

Consider now the heating of a medium carbon steel. At the Ac_1 point, i.e. at about 730° C., the pearlite changes to austenite; each pearlite grain, however, yields not a single austenite crystal, but an aggregate of very small crystals of varying orientations. As the temperature is raised the free ferrite is progressively taken into solution by the austenite, but the small-grained structure persists. At a temperature immediately above the ferrite line the structure consists of very small austenite crystals which again deposit ferrite on cooling. This ferrite is first deposited in exceedingly small quantity around some nucleus. If this nucleus lies within a large crystal of austenite, then further precipitation is along a crystallographic plane of that crystal. Since there are probably many more nuclei in each crystal, a lattice is initiated and further strengthened, giving rise to the Widmanstätten pattern already mentioned in connexion with cast structures. If, on the other hand, the steel is an aggregate of very small austenite crystals, the initial ferrite precipitation again takes place around nuclei; but since the austenite crystals are so very small, the first precipitation of ferrite may occupy the space of several of them. Thus there is established within the mass a number of nuclei of a prime order, more or less spherical in shape, and the final product is a microstructure of rounded masses of ferrite, small and evenly distributed, the pearlite filling the interspaces. Surface tension may also play some part in the shaping of these masses of ferrite.

It has already been indicated that steel is not sufficiently tough and gives low impact values when in the cast state. Ingot steels are toughened by forging and rolling, but with steel castings no mechanical work is possible. The Widmanstätten structure in castings may be modified considerably by the influence of silicon, but this brittle undesirable structure is only completely destroyed
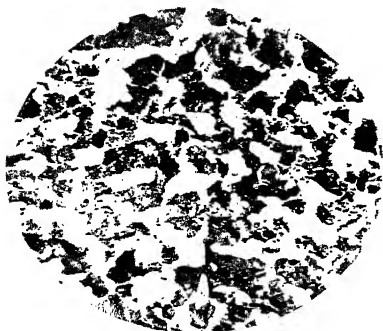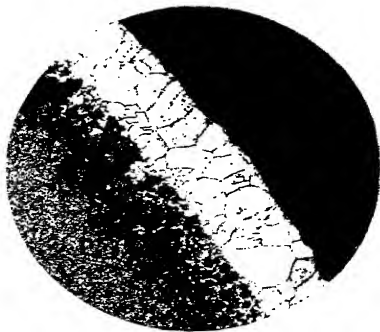
Fig. 81.—Steel casting in the cast state. ×50

Fig. 82.—The same casting after annealing at 900° C. ×50

Fig. 83.—High carbon steel rod—badly annealed. The surface layers are almost carbonless. ×60.

by the process of annealing. The annealing temperatures for steel castings are somewhat higher than those for worked steels, and are generally between 900° and 930° C. The higher temperatures yield coarser structures, but are necessary to ball up the sulphide membranes which, in the cast state, exist as thin films in the ferrite. These membranes exert a pronounced embrittling effect on the casting. The effects of annealing on the structure and properties of steel castings are illustrated by the micrographs shown in figs. 81 and 82 and the following tests:

	C.	Si.	Mn.	S.	P.
Composition	0·40	0·32	0·78	0·055	0·054

Condition.	Y.P., tons.	M.S., tons.	Elongation, per cent.	Reduction of Area.	Brinell No.	Impact, ft.-lb.	Bend.*
As cast	23·7	43·2	8·0	7·0	229	3	25° broken
Annealed at 900° C.	18·0	37·3	24·0	30·0	187	7	180° unbroken

Many forged steels are annealed in order to eliminate strains developed during working. Annealing softens the steel, which is therefore more easily machined. In many cases also, annealing is desirable in order to bring the steel into a suitable condition for subsequent heat-treatment.

Faults in Annealing.

In some cases the steel is packed in large cast-iron tubes, the open end afterwards being closed by a door, clay being used around the edges in order to exclude air during the time the furnace is being heated. This is known as " close-annealing ", as distinct from the more commercial " open " method where the steel is in contact with the actual heating chamber. Open-annealing, where the furnace gases and air come into contact with the steel, results in the oxidation of carbon in the outer layers. Drastic decarburization with the formation of a surface which is wholly ferritic may occur in extreme cases (fig. 83), and this seriously affects the properties of the steel, particularly when further heat-treatment is applied. An intelligent furnaceman, by the exercise of careful control over the character of the flame employed in heating, can often prevent the decarburization from becoming more than superficial, but the open-annealing of articles of thin section is most inadvisable. Steels which are close-annealed rarely show much

* ¾-inch radius

evidence of decarburization. In the annealing of steel castings, the open method is sometimes to be preferred for this reason. The moulds in which the metal is cast are " faced " with graphite which yields a highly carburized skin, and since this is brittle, it favours the development of incipient cracks. Open-annealing results in the decarburization of this outer skin, and even though the surface may then consist entirely of soft tough ferrite, this is of little or no disadvantage in most castings since it reduces the possibility of the production of minute surface cracks.

Under-annealing.—The annealing at too low a temperature of steels containing less than 0·89 per cent of carbon may be considered from two somewhat different aspects.

(*a*) When the temperature is between the upper and the lower critical points, the structure of the steel consists of austenite and some of the excess ferrite. This ferrite remains as a skeleton of the original unannealed structure, and when the steel is cooled the ferrite which has been taken into solution by the austenite is deposited around the masses of ferrite that remained undissolved. The tendency, therefore, is to reproduce the original unannealed structure.

(*b*) Annealing at temperatures below the lower critical point does not involve the formation of austenite, and hence no recrystallization occurs. The structure is not refined, and the original distribution of the ferrite and pearlite is unaffected, although a marked change in the structure of the pearlite itself may occur. The cementite lamellæ of the pearlite break up under the influence of surface tension forces, and assume globular forms giving rise to what is known as globular pearlite (fig. 84, facing p. 106). Globular pearlite seriously affects the tensile strength of the steel, and may result in the failure of parts which are placed in service without any subsequent heat-treatment.

This type of pearlite is also formed when steels are cooled very slowly throughout the range 700° to 650° C., and in many cases can be avoided by a somewhat quicker cooling shortly after the lower critical point has been reached. Very fine globular cementite is, however, more readily dissolved than the lamellar cementite of pearlite, and is therefore often to be preferred for needles, safety razor blades, and articles of thin section, since the time then required in heating for hardening is reduced to such an extent that decarburization does not occur so readily.

With very prolonged annealing below the lower critical temperature, coalescence of the minute carbide globules occurs, and in extreme cases the pearlite consists of comparatively large globules of cementite embedded in a ferrite matrix. This structure is known as " *divorced* " *pearlite*, and although the steel is certainly in its softest condition, this does not necessarily imply that it is in the best condition for machining. On the contrary, there is a marked tendency for the tool to dig into the soft ferrite and jump the hard cementite globules, and difficulty is then encountered in obtaining a good finished surface.

Drastically divorced pearlite is also undesirable in steels which are to be submitted to some further heat-treatment. The complete solution of the eutectoid cementite, upon which the success of such subsequent treatment depends, is then somewhat difficult. This is of extreme importance in connexion with the hardening of tool steels, and will be considered more fully later.

There are a few exceptional cases in which divorced pearlite is rather desirable than otherwise. For instance, steel sheets possessing this structure withstand repeated deformation much better than those in which the pearlite is distinctly laminated. It is important to bear in mind, however, that this divorcement of the pearlite is often associated with considerable decarburization if the steel has not been close-annealed.

Over-annealing, Overheating and Burning.—At temperatures just above the ferrite line, the structure of a steel consists of very small austenite crystals, but at higher temperatures some of these grow at the expense of others, crystal growth occurring much more rapidly as the temperature increases. The structure then consists of fewer but much larger crystals, and these deposit ferrite in comparatively large masses along the cleavage planes of the austenite as the steel cools. A gross structure of a somewhat Widmanstätten type is thus produced, and the material is then lacking in ductility and has little resistance to shock. Overheated structures of this type may be refined by reheating the steel to a correct temperature, although it is again more than probable that excessive decarburization will have occurred at the same time.

With a very high temperature, incipient fusion may occur in the outer layers. The decarburization is then very pronounced indeed, and oxide films may be formed in the grain boundaries of the ferrite or pearlite. Such a steel is described as being " burnt ",

and, unlike most overheated steels, cannot be restored or refined by any further treatment (fig. 85). Burnt steels are useless except as scrap for remelting.

Normalizing.

This process differs from annealing in the respect that the steel is allowed to cool down in air. The term is really a very loose one since thin sections cool rather quickly, whilst the rate of cooling of large masses may be so slow that their interiors show annealed or semi-annealed structures. Normalizing yields a much finer pearlite in which the laminations are not nearly so well marked as in the annealed steels. The tensile strength of " normal " pearlite is about 52 tons per square inch; consequently normalized steels have a much higher tensile strength than truly annealed steels of the same carbon contents. In addition, much better values are obtained for the yield-point and the reduction of area per cent, although the elongation per cent is not affected to any great extent. Many normalized steels give a much better surface after machining than the corresponding annealed steels. Rolled bars should always be normalized if circumstances permit, since the temperature at which the steel leaves the rolls has some influence on its properties. If the finishing temperature is low, the tenacity of the steel is raised, but the ductility lowered. Normalizing will then restore the ductility and ensure more uniform properties.

It will be evident that the properties of normalized steels are also influenced by the treatment temperatures. Thus fig. 86 shows a section from the fractured crankshaft of a slow-acting oil engine which failed after a very short life. The overheated structure is readily observed, and fig. 87 shows the same specimen after being reheated to a correct normalizing temperature.

Quenching, and its Effects on the Structure of Steel.

Martensite.—The general method for determining the structure of a metal or alloy at any given temperature consists in quenching a small specimen in some such medium as cold water. Rapid cooling tends to suppress normal transformations, and inhibits to an enormous extent the breakdown of solid solutions. The structure of the metal at an elevated temperature is therefore retained in some quenched specimens. Thus an α–β brass quenched from temperatures above 550° C. may be shown to consist entirely of the β solid solution when examined under the microscope. It
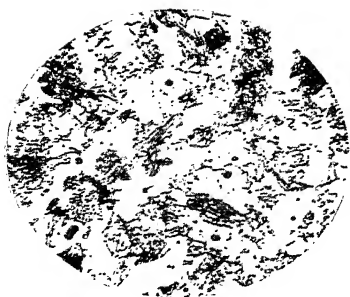
Fig. 84. — 0·5 per cent C steel (showing globular cementite) gave Yield-point, 19·9 tons; Max. stress, 37·4 tons; Elong. per cent (2″), 22·5; Reduction of Area per cent, 35·1. Compare these tests with those in table (p. 100). ×250.

Fig. 85.—" Burnt " nickel-chrome steel forging. × 50. Note the enormous grain size. The grain boundaries at higher magnifications are revealed as inter-crystalline cavities.

Fig. 86.—Section from overheated crankshaft. ⋏ 50

Fig. 87.—The same steel after a correct normalizing treatment. × 50

might be assumed, therefore, that the drastic quenching of a steel from the γ solid solution region would result in the preservation of the austenite. This does not happen, however, and austenite is only retained in carbon steels containing upwards of 1 per cent c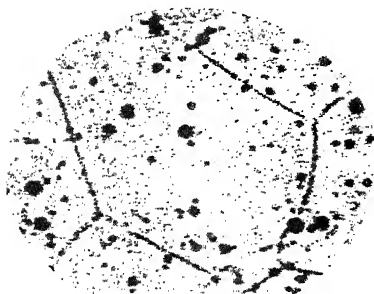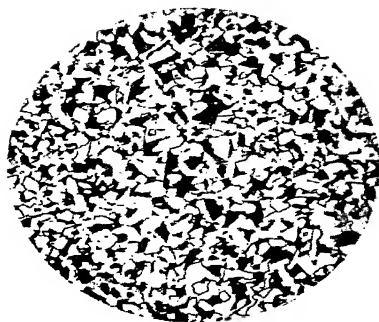arbon by the very rapid quenching of small specimens in ice-cold water from temperatures above 1000° C. Even this drastic treatment does not yield pure austenite, which is always associated with some other constituent. That quenching does have some influence on the structural transformations becomes quite clear, however, when rapidly quenched steels are examined under the microscope. The etched specimens then exhibit a fine interlacing needle-like structure known as *martensite* (fig. 88).

A 0·89 per cent carbon steel quenched from a temperature above the critical point consists entirely of martensite, and the steel then is in the hardest possible condition and will scratch glass. It is, however, very brittle, and has practically no ductility. Such a steel would have a Brinell hardness of at least 700 as against about 200 in the annealed (pearlitic) state. The hardening of steel is entirely dependent on the formation of martensite, since austenite is comparatively soft and ductile.

The real constitution of martensite has not been definitely established, but since martensitic steels are strongly magnetic, it must be assumed that part of the iron exists in the α form, and it has been suggested that martensite is a supersaturated solution of carbide of iron in α iron. The change from γ to α iron must therefore occur during quenching, and since in the time-temperature curves obtained during the operation there is evidence of a distinct recalescence at about 250° to 300° C., the change from austenite to martensite must be associated therewith. Further, since martensite is formed from austenite, a steel of any carbon content may be obtained in a wholly martensitic condition provided that it is rapidly cooled from temperatures above the *upper* critical point. The hardness of the martensite, however, decreases with decreasing carbon content, although the needles are generally more pronounced in the lower carbon steels.

A beginner will generally expect to find acicular markings in any martensitic steel, but the structure of the martensite is influenced to a very great extent by the temperature to which the steel is heated before quenching. A high temperature results in the formation of large austenite grains due to crystal growth; and, when quenched, the structure obtained is decidedly acicular.

explanation of its hardness. At these temperatures the mass is rigid, and tends to resist the volume changes associated with the breakdown of the austenite. The steel is then in a highly stressed condition, hence its hardness. On the other hand, troostite is formed at a temperature at which the material is more able to yield to any volume changes; consequently troostitic steels are more ductile but not nearly so hard.

Whereas martensite is formed as a result of the under-cooling of austenite, troostite is produced as the result of the inoculation of the solid solution by nuclei which are present in the steel. Excepting when very small specimens are used, the cooling by quenching of a low or medium carbon steel is not sufficiently rapid to prevent entirely the precipitation of ferrite whilst the steel passes through the ferrite range. The ferrite is deposited as microscopic particles more or less evenly distributed throughout the mass, and these particles then act as nuclei for the breakdown of some of the austenite, with the consequence that the microstructure consists of tiny ferrite particles enveloped by troostite in a background of martensite. This type of structure is obtained when the steel is quenched on a falling temperature, in which case a temperature gradient exists in the specimen at the moment of quenching. On the other hand, quenching on a rising temperature, in which case the outside of the specimen is hotter than the interior, generally yields a microstructure showing very little troostite even though some ferrite may be present. The formation of small amounts of troostite lessens the hardening stresses and reduces the risks of cracking and distortion, and in practical hardening one should always endeavour to quench on a falling temperature by slightly lowering that of the furnace (from 5° to 10° C.) just before quenching.

Sorbite.—When the rate of cooling is intermediate between those required to yield troostite and pearlite, the particles coalesce and are visible under the microscope. Such a structure is called sorbite, and the various stages in the transformation of austenite into pearlite may therefore be represented in the following order according to the rate at which the steel is cooled:

Austenite—Martensite—Troostite—Sorbite—Pearlite.

Effects of Tempering on Quenched or Hardened Steel.

Most engineering steels, after being hardened, are subjected to some tempering treatment, i.e. reheated to a temperature which

is always *below the lower Ac point*. The explanation of the structural changes involved will perhaps be somewhat simplified by reference to the heating curve of a hardened 0·89 per cent carbon steel (fig. 90), from which it is clear that a marked evolution of heat occurs, as indicated by the slope of the curve to the left, until a temperature of 450° to 500° C. is reached. The energy previously stored up in the martensite and troostite is then dissipated in the form of heat, and the structure consists entirely of cementite and
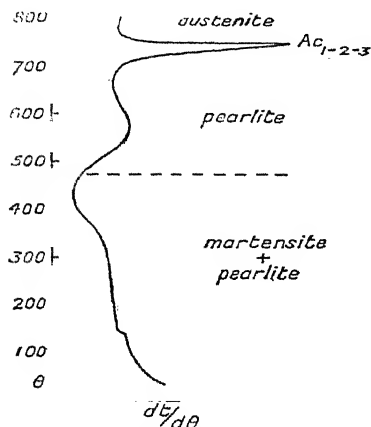
ferrite. Since in this instance a 0·89 per cent carbon steel is being considered, this structure may be regarded as a form of pearlite, but the term is only applicable to steels of this carbon content. Such a steel is said to be fully tempered, and at temperatures higher than 500° C. the material remains in the pearlitic state until the Ac_{1-2-3} point is reached, when austenite is reformed. It is thus clear that the tempering of a hardened steel results in a breakdown of the martensite at a comparatively low temperature, at which the steel is rigid and its internal viscosity high. In the earlier stages of this breakdown the carbide particles are ultra-microscopic, and although some coalescence will occur when the steel is fully tempered, the fine structure is still more or less retained. The carbide is readily discerned under the microscope at high magnifications as tiny globules embedded in a ferrite matrix. Such a structure is a true *sorbite*, or, in the case of a eutectoid steel, sorbitic pearlite. Sorbite is the constituent present in all quenched and fully tempered steels. When the steel is tempered above 550° C., the carbide particles coalesce to such an extent that the structure is not nearly so fine.

With steels containing less than 0·89 per cent carbon, analogous changes occur, but there will obviously be a smaller number of carbide particles in the specimen. The distribution of the carbide

Fig. 90.—Heating Curve of Quenched 0·89 per cent Carbon Steel

is very uniform, however, and quenched and fully tempered steels appear to contain a higher carbon content than is actually the case, as will be evident from fig. 91 (facing p. 108), which is a micrograph of a steel containing 0·63 per cent carbon and 0·44 per cent manganese, a small specimen of which was quenched in water from 790° C. and tempered at 500° C.   The effect of tempering at different temperatures on the mechanical properties of steel is indicated by the following figures:

Composition of steel: C, 0·34; Si, 0·13; Mn, 0·47; S, 0·06; P, 0·04.

All test-pieces (0·564″ diameter) quenched in water from 830° C.

Tempering Temperature.	Y.P., tons.	M.S., tons.	Elongation (2″), per cent.	Reduction of Area, per cent.	Brine No.
Untempered:	47·9	62·0	3·5	7·7	·262
200° C.	45·0	56·3	8·0	29·4	217
300° C.	42·2	48·5	9·0	36·7	212
400° C.	40·3	50·0	17·5	50·7	223
500° C.	41·4	48·9	21·5	57·2	201
600° C.	30·8	40·4	22·0	60·8	183
700° C.	26·3	34·7	32·0	66·2	174

The excellent properties of sorbite are well illustrated by the above tests on the specimen tempered at 500° C.   Sorbite is indeed the constituent most desirable in highly stressed parts, since sorbitic steels are characterized by a truly remarkable combination of tensile strength, ductility, and resistance to shock.   When the steels are tempered above 500° C., the tensile strength falls rapidly with no marked improvement in the ductility.   Tempering at lower temperatures than 500° C. is generally carried out with the object of diminishing the excessive brittleness generally associated with quenched steels.   Tool steels are generally submitted to a low temperature treatment for this object alone.   A mild tempering treatment when applied to the quenched lower carbon steels, such as those used as crankshafts, results in a considerable improvement in the ductility whilst a high tensile strength is still retained.

Quenching Media.

The liquids in general use for the hardening of steel are water and oil.   The oils commonly employed are whale oil and such vegetable oils as cotton and rape. Whale oil is comparatively cheap, its greatest disadvantage being its abominable smell when rancid. Cotton-seed oil has a much less disagreeable smell and does not turn rancid, but is rather too viscous at ordinary temperatures.

It is therefore usually mixed with a smaller proportion of some mineral oil of higher mobility.

Water is obviously the cheapest quenching medium, and is invaluable for tools and purposes where an extremely hard surface is desired. In the latter case, the desired effect may sometimes be obtained by spraying the surface with a sufficient volume of water. The disadvantage associated with water-quenching is the tendency to cause cracking and distortion. With low carbon steels, these risks are not very great if the materials are of uniform thickness; and water-quenched steels, when fully tempered, generally yield better tests than those which are oil-quenched and tempered.

Oil, owing to its lower thermal conductivity and heat capacity, does not exert such a drastic quenching effect, with the consequence that fair quantities of ferrite and troostite are observed even in small sections of quenched low and medium carbon steels. During quenching the temperature falls more slowly than when water is employed, and the articles should be continuously moved about in the quenching bath until they are quite cold, otherwise vapour collects around them, and the cooling is further retarded with a consequent lowering of the ultimate tensile strength and hardness. So far as the mechanical tests are concerned, oil-quenching is equivalent to a water-quenching plus a mild tempering.

For many engineering materials, such as axles, crankshafts, and other railway requisites, sorbitic steels are required. Two methods of heat-treatment are adopted, viz. (a) normalizing, and (b) oil-quenching and tempering. The better results obtained by the second method are obvious from the inspection of the tests given below, and the micrographs shown in fig. 92 (a) and (e). It is almost impossible by normalizing even small sections to obtain a microstructure which is entirely sorbitic when the carbon content is less than 0·6 per cent. Better results are generally obtained with a higher manganese content, and for this reason manganese is generally present in greater quantity in steels which are to be normalized only.

Composition of steel: C, 0·29; Si, 0·05; Mn, 0·52; S, ·047; P, ·033.

Treatment.	Y.P.	M.S.	Yield Ratio, per cent.	Elonga- tion on 2″.	Reduction of Area.	Brinell No.
(a) N. 825° C.	21·2	33·2	63·7	31·5	60·9	150
(b) W.Q. 825° C.	42·2	63·3	66·7	1·5	2·9	285
(c) W.Q. Td. 575° C.	34·6	44·0	78·4	21·5	59·7	200
(d) O.Q. 825° C.	28·4	40·3	70·5	22·5	60·4	180
(e) O.Q. Td. 575° C.	26·2	38·6	67·8	26·5	60·9	175
(f) Ann. 825° C.	17·4	30·8	56·0	30·0	53·9	130

(a) Ferrite and pearlite
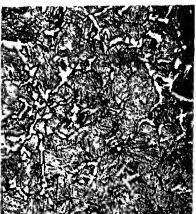
(b) Ferrite enveloped by troostite in martensite matrix
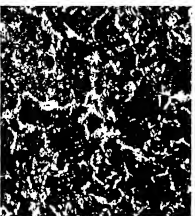
(c) Ferrite and sorbite
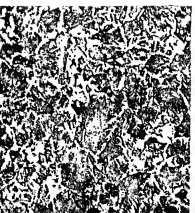
(d) Ferrite with troostite (black) in martensite matrix

(e) Ferrite and sorbite

(f) Ferrite and pearlite

Fig. 92.—Micrographs of specimens of given composition after being subjected to treatments given in table on p. 112. All magnified 250 times

E 428

(a)   (b)   (c)   (d)   (e)   (f)

Fig. 93.—Fractures of tensile test-pieces subjected to the treatments specified in the table on p. 112

The appearance of the fracture of a tensile test-piece is often a good indication of the properties of the steel, and a " cup and cone " fracture is usually associated with good material in the best condition for many purposes such as those specified. Fractures, such as those shown in fig. 93, should therefore be carefully observed and correlated with the mechanical tests and microstructures.
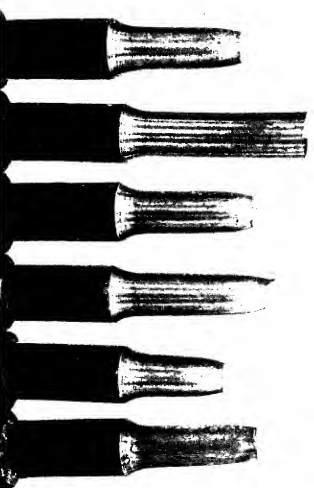
It will be observed that annealing seriously affects the yield-point, and that this value is very much improved by quenching and tempering. In addition, this treatment yields good values for the reduction of area, which can generally be associated with good fractures and high impact figures. The reduction of area per cent is a much better criterion of the properties of heat-treated steel than is the elongation.

The tests on the fully quenched specimens have been included above merely for the sake of completeness, but the micrographs show that the distribution of the free ferrite in the hardened specimens is practically unaffected by tempering.

Effect of Mass on Heat-treatment.

The size of the piece treated exerts some influence on the properties of heat-treated steels. This influence is most marked in quenched steels, and much better test results are generally obtained when comparatively small pieces are being dealt with. This must always be considered when a steel is being selected for some specific purpose, since the figures generally given to indicate the properties of the material are the results of tests carried out on heat-treated bars of about 1 in. to $1\frac{1}{4}$ in. diameter, and much thicker sections cannot be expected to yield identical values when subjected to similar treatments. Bullens * gives the following figures as being representative of the effect of mass on the tensile strength:

Diameter of bar (in.)	$\frac{1}{2}$	1	$1\frac{1}{2}$	2	$2\frac{1}{2}$	3	$3\frac{1}{2}$
Max. stress (tons per sq. in.)..	63	60	58	55	50	48	45

The influence of mass thus becomes a factor of very real importance in the treatment of large forgings. Even when quenched in water, the interior of a large mass may cool so slowly that the structure consists of ferrite and pearlite, although the surface layers are essentially martensitic. A very decided variation in

* *Steel and its Heat-treatment* (Chapman and Hall).

structure and properties from the surface to the centre of any large mass is therefore inevitable. This difference in structure is clearly indicated in fig. 94 (*a*), (*b*), and (*c*).

It has already been stated that the distribution of the constituents in a quenched steel is practically unaffected by tempering, and the mass effect thus persists in the fully tempered specimens. This is evident from the micrographs shown in fig. 95, and from the following data:

Composition of steel: Carbon, 0·31 per cent.
Silicon, 0·18 per cent.
Manganese, 0·5 per cent.
Sulphur, 0·056 per cent.
Phosphorus, 0·029 per cent.

Each specimen was heated to 850° C., quenched in water, and then fully tempered at 600° C.

Size of Piece Treated.	Relative Area of Cross-section.	Y.P.	M.S.	Elongation.	Reduction of Area.	Brinell No.	Impact.
0·968″ diameter	1·0	28·9	38·6	28·0	65·5	163	55, 55
1·188″ ,,	1·5	25·0	36·2	30·5	66·5	152	62, 65
1·625″ ,,	2·8	24·2	36·0	30·0	65·0	149	52, 55

The effects of mass can be somewhat minimized by one of the following methods: (*a*) By using steels of slightly different composition although employing similar heat-treatment temperatures, or (*b*) using the same steel but employing higher quenching or normalizing temperatures for the more massive parts.

The tensile strength of a steel containing less than 0·5 per cent of carbon may be increased without seriously affecting its ductility by quenching or normalizing from about 20° C. above the usual treatment temperatures. Much higher temperatures are not to be recommended, however, and in a steel containing more than 0·5 per cent carbon even this degree of overheating may seriously affect the ductility. If circumstances permit, it is more satisfactory to alter the composition of the steel to suit the mass which is to be treated, steels of slightly higher carbon and manganese contents being employed for the larger sections.

The time taken to heat the steel also obviously depends on the mass. Sufficient time must be allowed for transference of heat to the interior, and since a considerable quantity of heat is necessary to dissolve the iron carbide and thus yield austenite, this also has a marked influence on the total time taken. Few reliable quantitative data are available, and the curves given in
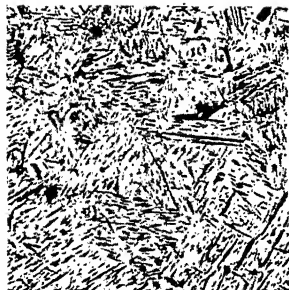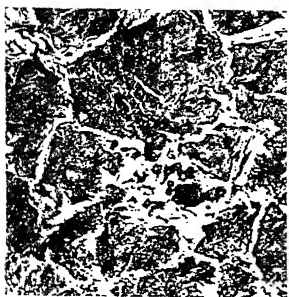
(a)   (b)   (c)

Fig. 94.—Illustrating the effect of mass on the structure of a steel bar 1⅜″ diameter containing 0·3 per cent carbon, 0·5 per cent manganese, after quenching in water from 840° C.

(a) Near surface—practically all martensite. Vickers diamond hardness 525.
(b) About ¾″ below surface—martensite and streaks of ferrite in troostite matrix. Vickers hardness 327.
(c) Centre of bar—ferrite and troosto-sorbite. Vickers hardness 212. All magnified 250 times.

(a)   (b)   (c)

Fig. 95.—Micrographs of steel containing: ___, 0·31 per cent; Silicon, 0·18 per cent; Manganese, 0·5 per cent; Sulphur, 0·056 per cent; Phosphorus, 0·029 per cent; W.Q. 850° C.; Td. 600° C.

(a) Treated in 0·968″ diameter. (b) Treated in 1·188″ diameter. (c) Treated in 1·625″ diameter. × 250

fig. 96 for cylindrical bars can only be regarded as having a very general significance. These curves have been constructed on the assumption that the temperature of the furnace remained constant both before and during the whole of the time the bars were in the furnace.   The influence of the pearlite-austenite change is clearly indicated by the considerable differences in the times taken to
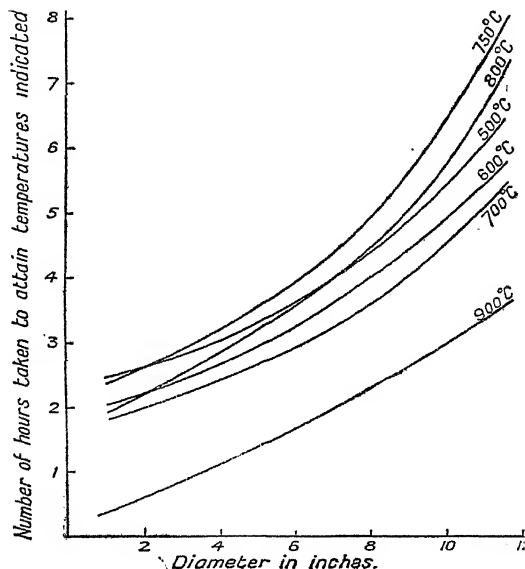
Fig. 96.—Showing Effect of Mass on Time required for Thorough Soaking

heat the steel to 700° and 750° C., but apart from this effect it will be observed that the time required to attain a uniform temperature throughout decreases with a higher furnace temperature.   This would be expected, since a steeper temperature gradient exists in the specimens under such circumstances, and in accordance with the laws of thermal conductivity heat flows to the interior at a more rapid rate.

The following hints on practical heat-treatment will perhaps be appreciated.

Heating.

The temperature of the furnace before the articles to be treated are placed in it should not be far removed from the actual treatment temperature. A shorter time is then required for soaking, and the tendency towards decarburization is decreased. The higher carbon steels, however, may crack if suddenly placed into a very hot furnace, and for this reason. The outer layers attain the temperature corresponding to the lower critical point whilst the interior is still comparatively cool and rigid; hence the material is not in a suitable condition for withstanding the stresses impressed upon it as the result of the volume changes accompanying the pearlite-austenite change in the outer layers. It is therefore advisable to heat such steels more slowly at the front of the furnace, or better still, in another furnace at a lower temperature, until the articles are at a dull red heat.

The door ends of the treatment furnace will generally be at a somewhat lower temperature than the interior; forgings of varying section should therefore be placed so that the thicker parts are in the hottest zones.

Long cylindrical objects should be rolled over and turned about in order to ensure a uniform temperature throughout and thus minimize the risks of cracking and distortion when the articles are quenched.

Practically all modern heat-treatment shops are fitted with thermo-electric temperature indicators, but it is not always realized that periodic calibration is necessary even with the most elaborate platinum thermocouple installations. For this purpose, the freezing-point of common salt is a very convenient standard temperature. Ordinary " rock salt " is cheaper, and, for this purpose, better than the specially prepared table salts containing other substances intentionally added which may lower the freezing-point to an appreciable extent. The salt is melted in an iron pot, and the pyrometer is placed in the clear liquid, which is then allowed to cool. When the salt freezes, the instrument should indicate a temperature of about 800° C. If the error is within $\pm 10°$ C., this may be allowed for, but if outside these limits, the thermocouple should be discarded and a new one substituted, since further and more serious deterioration may rapidly take place.

A further important point is to observe that the end of the

pyrometer protecting sheath is as close as possible to the articles which are to be treated. An excellent method consists in stacking the articles around the thermocouples, which are then almost long enough to reach the floor of the heating chamber.

The materials are conveniently inspected from time to time through small peep-holes in the furnace doors, and when thoroughly soaked the steel and the heating chamber have the same uniform tint.

Quenching.

Precautions having been taken to ensure a uniform temperature throughout, the material is gripped in such a manner that the whole mass may be quenched as quickly as possible. The thicker parts of articles of varying section should enter the quenching medium first. Hardening strains are then decreased and a more uniform quenching effect obtained.

Long cylindrical objects should be quenched vertically, whilst discs and flat sections are more satisfactorily quenched edgeways. Rings may be gripped at two diametral points and rapidly but carefully quenched, so that each point on the lower surface enters the quenching bath at the same instant.

Unless the greatest care is taken in quenching, warping readily occurs, and even if the steel does not crack during the actual quenching operation, it may do so when subsequently straightened.

Distortion is considerably reduced by using quenching machines such as those used in the heat-treatment of some water-hardened cranks.

It has been shown that steel cubes, after repeated quenchings, tend to assume spherical shapes, and a certain amount of distortion is therefore always to be expected. Although this distortion, after a single quenching, is so slight as to cause little trouble, it is evident that articles of almost finished size should be subjected to as small a number of reheatings as possible.

In some cases, particularly when larger masses are being dealt with, oil-quenching may not be sufficiently effective, whilst on the other hand water-quenching may be much too drastic. A combination of both methods may then be employed, both liquids being contained in the same tank, the oil, by virtue of its lower specific gravity, floating on top of the water. The article to be quenched is then plunged into the oil, kept there for several seconds, and afterwards lowered into the aqueous layer below. The

first quenching is thus a comparatively mild one, and the intensity of the quench in the water is decreased as the result of the oil films on the surface of the steel. An effective quench is therefore possible without any great risk of abnormal distortion.

In all quenching operations a sufficient volume of liquid should be used so that the temperature of the bath is not raised more than a degree or so, particularly when several articles are quenched in sequence; since a pronounced rise in the temperature of the quenching medium may lower its efficiency to a very appreciable extent. Hot water is indeed often intentionally employed for some of the higher carbon steels in order to minimize the risk of cracking.

Tempering.

For temperatures below 350° C. special oils having a high flash-point may be employed. For higher temperatures, and in cases where it is only desired to temper certain parts of the quenched object such as the threaded parts of screws, molten lead forms a very effective tempering bath. For still higher temperatures and for larger masses, gas furnaces are commonly employed.

The mass effect must also be considered in tempering, and on this account large forgings, shafts, &c., are often bored out previous to heat-treatment. The final structure, after tempering, is then much more uniform and the material stronger, even though of lesser mass, than if the boring operation were omitted.

A quenched steel is really in a very highly stressed condition, and in many cases a low temperature tempering treatment is applied to diminish the intensity of the stress and thus prevent the belated cracking which sometimes occurs many hours afterwards in certain types of hardened steel. Such steels should therefore be tempered immediately after hardening.

CHAPTER V

" Special " Steels and other Ferrous Alloys

" Special " or alloy steels contain, in addition to iron and carbon, notable quantities of one or more of the following elements: nickel, chromium, manganese, silicon, cobalt, tungsten, and vanadium. Some of these form solid solutions with both α and γ iron, and this results in increased strength and toughness; others combine with carbon to yield carbides of exceptional hardness and stability. The effect of each element is very conveniently studied by its influence on the iron-iron-carbide equilibrium diagram. The principal effects generally observed are as follows:

(a) The quantity of carbon required to form pearlite is generally lower in alloy steels than in carbon steels. Thus steels containing about 0·7 per cent carbon with either 1 per cent manganese or 3·5 per cent nickel consist entirely of pearlite in the annealed states.

(b) Alloying elements alter the positions of the critical points, and the heat-treatment temperatures for alloy steels are generally somewhat different from those for carbon steels.

(c) The critical transformations are retarded, and alloy steels, in general, possess lower critical hardening speeds, with the consequence that the effect of mass is less pronounced than in carbon steels. Greater uniformity of structure is thus obtained in large masses.

As a result of (b) and (c) many alloy steels can be obtained in a martensitic condition by a much milder form of quenching, such as quenching in oil, or in some cases by simply cooling in air, and the beneficial effects thus conferred will be readily appreciated since the risks of cracking and distortion are reduced to a minimum.

Some steels, containing large quantities of the alloying elements, may even be retained in the austenitic condition at ordinary temperatures. Such steels are often characterized by exceptional resistance to corrosion and abrasion.

Chromium Steels.

Chromium readily alloys with iron, and is also capable of existence in solid solution with either α or γ iron. In most steels, however, the element exists in combination with carbon as chromium carbide Cr_3C_2. The iron in the carbide of iron is not completely displaced, but solid solutions of the two carbides are formed, and the resulting double carbides are very hard and stable. Small quantities of chromium are indeed introduced into many of the higher carbon steels, to render the carbide more stable, and thus prevent graphitization during working and annealing.

1 per cent of chromium increases the tensile strength of a 0·5 per cent carbon steel by about 10 tons per square inch, without, however, decreasing the ductility to any appreciable extent. This element also improves the wearing properties of the steel, and even in the low chromium steels some improvement in the resistance to corrosion is obtained.

The quantity of carbon required to yield pearlite gradually decreases with increasing amounts of chromium. Thus steels containing 1·35 per cent Cr, 0·7 per cent C; 2·8 per cent Cr, 0·62 per cent C; 14 per cent Cr, and 0·35 per cent C consist entirely of pearlite in the slowly cooled states. Chromium raises the Ac points in steel, and when slowly cooled the Ar transformations also occur at higher temperatures than those for carbon steels of corresponding carbon content. More rapid rates of cooling, however, result in a depression of the Ar points, with the consequence that chromium steels are, to some extent, self-hardening. The introduction of chromium into steel has one serious drawback, due to the tendency for the element to promote excessive grain growth during heating. This crystal growth may take place to an alarming extent when the steels are overheated, and even after prolonged heatings at normal heat-treatment temperatures. Such steels are then exceedingly brittle. Consequently, if chromium is the only alloying element present, the greatest care must be exercised in the heat-treatment of these steels if the most satisfactory results are to be obtained; and for this reason, chromium is often associated with either nickel, tungsten, or vanadium, elements which tend to inhibit grain growth and do not counteract the beneficial effects due to the chromium.

Steels containing about 1 per cent chromium and 0·2 per cent

vanadium have found extensive application in America for some engineering purposes, but are not nearly so popular in this country. The composition of such a steel and its properties in the heat-treated condition are as follows:

C.	Mn.	Cr.	V.	Y.P.	M.S.	Elongation.	Reduction of Area.	Brinell No.	Impact.
0·35–0·45	0·5–0·8	1–1·5	0·1–0·25	44–60	60–80	12–20	45–65	241–311	45–85

Treatments: O.Q. 840°–870° C.: Td. 550°–650° C.

The steels of the lower carbon and chromium contents are used for axles, crankshafts, connecting-rods, &c., as rivals to the nickel-chrome steels, the advantages claimed being that such steels are easier to work than many Ni-Cr steels, and simpler and less delicate heat-treatments are required. These statements must, however, be accepted with reserve, since there is no doubt that a properly heat-treated nickel-chrome steel of suitable composition gives better results for the purposes specified. The steels of the higher carbon and chromium contents, after being tempered at the lower temperatures, are used for springs and gears, whilst a steel of a somewhat similar type is used for armour-piercing shells.

About 1 per cent Cr has also been introduced into some rail steels with very encouraging results in service. The effect of chromium on the properties is clearly indicated by the following data, due to Swinden and Johnson.[*]

Typical Acid O.H. steel rail.
Composition: C, 0·53; Si, 0·11; Mn, 0·88; S, 0·038; P, 0·037.

Falling Weight Test (1 ton tup).

Height of fall (ft.)	7	20
Deflection (in.)	0·8	3·1

M.S.	Elongation.	Reduction of Area.	Brinell No.
51·3	14·0	18·6	231

Acid O.H. chromium steel rail.
Composition: C, 0·51; Si, 0·176; Mn, 0·83; S, 0·03; P, 0·037; Cr, 1·61.

Falling Weight Test (1 ton tup).

Height of fall (ft.)	..	6	18	18	18	12
Deflection (in.) ..	..	0·6	2·4	4·2	6·0	7·1

M.S.	Elongation.	Reduction of Area.	Brinell No.
59·9	15·5	36·7	277

* *J.I.S.I.*, 1928 (i).

Steels containing higher proportions of carbon generally contain free carbide, and the heat-treatments are somewhat similar to those employed for tool steels, although the treatment temperatures are different. Even a very small amount of chromium apparently induces that pronounced spheroidization of the hypereutectoid cementite which is so desirable in such steels. Ball-bearing and ball-race steels are greatly improved by as little as 0·25 per cent of the element, the toughness and resistance to wear being increased without detriment to the hardness.

The highest grades of ball-steel contain 1 to 1·5 per cent chromium, and sometimes 0·25 to 0·5 per cent tungsten also, to yield a finer grain. These steels are characterized by their extreme hardness and high crushing strengths. Uniformity in structure is essential in ball-steel, and the material should not show any " soft spots ". In addition, the steel must be clean, i.e. free from slag and other inclusions. For these reasons, chromium steels of this class are generally made in furnaces of comparatively small capacity. The steel must be cast with great care, otherwise it is particularly liable to fine hair cracks on the surface if improperly treated. A long soaking is required before forging, and a prolonged annealing is necessary to " ball up " the free carbide before the material is hardened. Ball-steels are generally hardened by quenching in oil from about 830° C., and in some cases the hardness is still further increased by subjecting the materials to cold-work. Thus steel balls are often greatly overloaded intentionally, and after running for some time a considerable increase in the hardness is obtained, although the material is very hard to commence with. Steels of similar composition are employed in stone-crushing machinery and for rolls for steel and non-ferrous metals.

Steels containing more than 2 per cent each of carbon and chromium are used for drawing dies for wire, where a hard material extremely resistant to wear is required. These dies, as the holes wear, are subjected to repeated heatings and hammerings which tend to induce decomposition of the hard carbides. Chromium is added in comparatively small amounts (up to 2·5 per cent), mainly to overcome the tendency for such high carbon steels to undergo graphitization. The highest qualities contain up to 12 per cent of the element, the metal then conferring increased strength, hardness, and resistance to wear.

Analyses of some commercial high carbon chromium-steels are given on the following page:

C.	Si.	Mn.	S.	P.	Cr.		Uses.
1·40	0·15	0·35	0·025	0·025	0·50		Ordinary razors.
1·10	0·15	0·40	·025	·025	0·25		Ball-bearings.
1·05	0·15	0·40	·025	·025	1·25–1·5		Ball-bearings, crushing machinery, and cold rolls.
						w.	
1·10	0·15	0·35	·025	·025	0·5	0·5	Hack-saw blades.
2·25	0·25	0·50	·030	·030	2·0		Cold rolls and drawing dies.
2·00	0·25	0·60	·030	·035	10·0		Cold rolls and drawing blanking dies.
0·75	0·20	0·40	·030	·030	·50		Chisels.
0·90	0·15	0·60	·030	·025	·60		Pneumatic chipping chisels.
0·90	0·15	0·50	·035	·030	3·50		Permanent magnets.

Nickel-iron Alloys.

Although nickel is generally regarded as a ferromagnetic substance, it is interesting to note that it has a magnetic change-point at about 365° C. analogous to the α–β change in iron. Nickel readily alloys with iron, and the resulting solid solutions would be expected to possess a magnetic change-point. Commencing with pure iron, the temperature at which each alloy recovers its magnetic properties is found to decrease as the amount of nickel increases up to nearly 30 per cent, when the transformation occurs at about 0° C. On heating, however, the magnetic changes do not occur until much higher temperatures are attained, and this lag may amount to as much as 300° C. Certain iron-nickel alloys may thus be obtained in either a magnetic or a non-magnetic state at ordinary temperatures. Such alloys are said to be " irreversible " in order to distinguish them from the " reversible " alloys containing upwards of 30 per cent nickel, in which the magnetic changes on heating and cooling occur at the same temperatures.

30 per cent nickel alloys are austenitic at ordinary temperatures after normal cooling, and are therefore non-magnetic. Although stable at ordinary temperatures, these alloys can be obtained in a martensitic state by quenching in liquid air, when they become magnetic and remain so when again allowed to attain ordinary temperatures. In the austenitic (non-magnetic) state, a 30 per cent nickel alloy has an expansibility approximately equal to that of brass, whilst in the magnetic condition the coefficient is of the same order as that of iron.

The reversible alloys containing more than 30 per cent nickel, however, have definite expansibilities whatever may have been the temperatures to which they have been previously submitted.

The coefficients of expansion of the iron-nickel alloys decrease

with increasing nickel contents, until a definite minimum value is obtained at about 36 per cent nickel, an alloy of this composition possessing a small negative coefficient. Such alloys are known as *Invar metal*, a typical composition being 0·5 carbon, 0·5 manganese, and 35 to 36 per cent nickel. As ordinarily obtained, Invar is unstable, and if a bar is left to itself, is found to increase in length. This expansion is, however, a logarithmic function of the time, and hence, at ordinary temperatures, may take years to complete itself. This " ageing " effect appears to be intensified by carbon, and in view of the difficulties involved in manufacture in keeping a very low carbon content, almost all alloys of the Invar type exhibit this phenomenon to some extent. The errors due to " ageing ", however, have been reduced to a minimum by maintaining the alloy at 100° C. for several days and then cooling down very slowly over a period of several months.* The expansion due to ageing is permanent.

The relative expansibilities of platinum, Invar, and a 0·6 per cent carbon Bessemer steel are as follows:

Variation in Length (microns).	Platinum.	Invar.	0·6 C. Bess. Steel.
at 10° C.	88·6	+0·05	121
at 20° C.	177·6	—0·36	242
at 30° C.	266·9	—1·26	364

Applications of Invar.—Invar is extensively employed in time-measuring instruments, particularly where great accuracy is required. It is also used for tape and wire measures, and in surveying, since generally no temperature corrections are necessary. A more recent application of Invar is in connexion with the development of aluminium alloy pistons of special split construction. Invar is then employed in such a manner that the net thermal expansion is almost equal to that of cast iron. The advantage of the light piston is thus retained without risk of seizure due to excessive expansion.

Permalloy.—This contains about 78·5 per cent nickel and 21·5 per cent iron, carbon and sulphur being kept as low as possible. Permalloy is characterized by its extremely high permeability in low magnetic fields. Thus, with a field strength of 0·05 Gilberts, when the alloy is properly treated, the permeability is about 90,000 as against 5000 for either iron or silicon-transformer steel at the same field strength. The hysteresis loss is abcut one-fifteenth

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* Guillame, *Mond Nickel Bulletin*, A.2

of that of pure iron. Permalloy is used in the loading of submarine cables where a high permeability for low field strengths is essen-
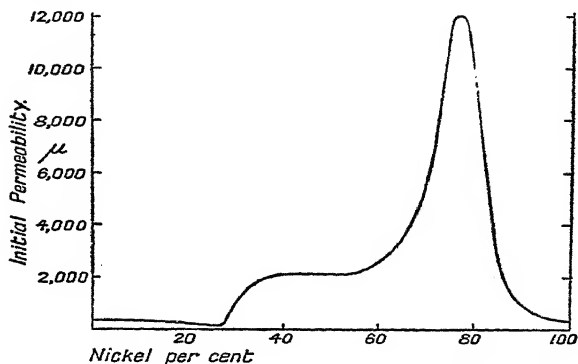

Fig. 97.—Showing Effect of increasing Nickel Content on the Permeability of Nickel-iron Alloys

tial, and it is claimed that the use of this alloy has resulted in an increased rate of cable communication from 300 to 1500 signals
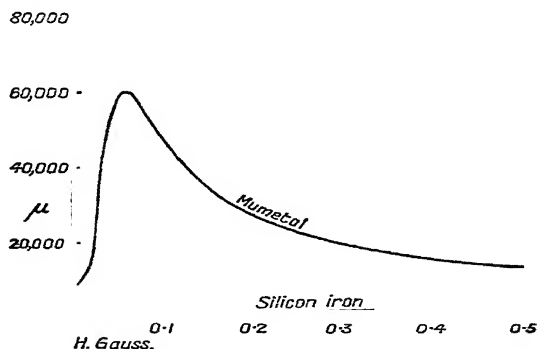

Fig. 98.—μ-H Curves for Mumetal and Silicon Iron (Telegraph Construction and Maintenance Co., Ltd.)

per minute. The alloy must, however, be handled with care, since if much stress is put upon it after it has been heat-treated, the magnetic properties are very seriously impaired. " Over-strain "

decreases the permeability and increases the hysteresis loss. The best properties are obtained by heating to 900° C., cooling slowly, and then reheating to 600° C., finally cooling in air.

The relationship between permeability and nickel content is shown in fig. 97, and it will be observed that Permalloy has a critical composition, slight variations on either side of this critical value resulting in a marked falling-off in the permeability.

Mumetal.—Another alloy of a similar type is known as " Mumetal ", which contains an appreciable quantity of copper and some manganese, the following composition being typical: Nickel, 74 per cent; Iron, 20 per cent; Copper, 5·3 per cent; Manganese, 0·7 per cent. The latter two elements cause an increase in the electrical resistance with a consequent lowering of the eddy current losses, whilst the manganese also confers improved forgeability. μ–H curves for annealed Mumetal and a commercial iron-silicon steel are given in fig. 98, from which it will be observed that the iron-nickel alloy is almost saturated in the earth's field.

Nickel Steels.

Carbon is an essential constituent of nickel steel, and since nickel tends to promote graphitization of the carbide of iron, some
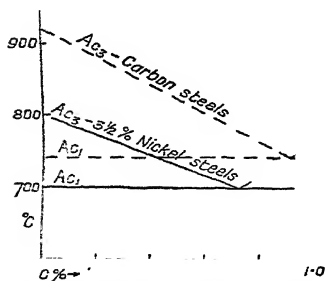

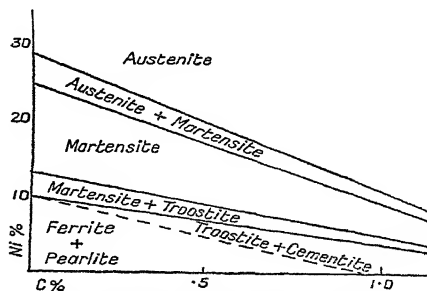Fig. 99.—Showing Effect of 3·5 per cent of Nickel on the Critical Points of Steel

Fig. 100.—Showing the Effect of Nickel on the Constitution of Annealed Steels (Guillet)

other element is necessary to inhibit this tendency and render the carbide more stable. " Plain nickel " steels thus contain fair quantities of manganese, as much as 0·8–0·9 per cent being found in those of the lower carbon contents. Silicon is also present, and electric furnace steels may contain as much as 0·35 per cent of this element. Both manganese and silicon are necessary to ensure

comparative freedom from oxide of iron. Nickel exerts a very marked effect on the critical transformations in steel. This effect is indicated in fig. 99, whilst the constitutions of the slowly cooled alloys are shown in the diagram (fig. 100), due to Guillet, which, although not strictly accurate, will serve as a general indication.

The most useful engineering nickel steels are pearlitic when slowly cooled, readily yield to heat-treatment, and give a wide range of mechanical properties. Steels containing less than 0·5 per cent carbon and 5 per cent nickel, forge as well as, if not better than the corresponding carbon steels. Above 5 per cent nickel, however, the steels are tougher and more difficult to forge, and few steels containing more than 7 per cent nickel are employed for general structural purposes.

The most popular nickel steels are those containing between 3 and 4 per cent nickel and 0·25–0·4 per cent carbon, although steels of somewhat lower nickel content (2·5–3 per cent) are sometimes preferred for some drop forgings. Most of these steels are used in the oil-quenched and fully tempered state.

Fig. 101.—Inverse-rate Curves of a Steel containing Carbon, 0·37 per cent; Manganese, 0·66 per cent; Nickel, 3·65 per cent.

Nickel increases the strength without affecting the ductility, and in a 0·25 per cent carbon steel the maximum stress is increased by about 2–2·5 tons per square inch for each 1 per cent nickel addition.

Typical heating and cooling curves are given in fig. 101. It has been shown, however, that the initial temperature to which many alloy steels are raised before quenching exerts a marked effect on their properties, and in order to obtain the greatest hardening effect it is necessary to heat the materials to temperatures well above their critical ranges. Nickel, however, diffuses slowly in the solid state, and this slow rate of diffusion hinders grain growth. The overheating of a nickel steel does not therefore exert so harmful an influence on its properties as on those of the nickel-free steels. Temperatures about 100°–200° C. above the critical points on heating are generally employed, but in view of the lowering of the Ac points by the nickel, the heat-treatment temperatures do
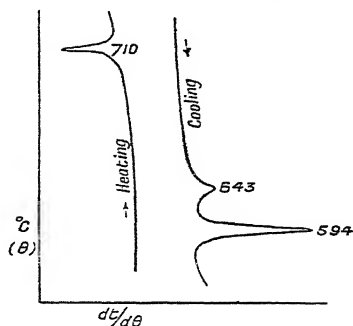
not differ appreciably from those for the nickel-free steels of the same carbon contents.

The usual softening treatment for a 0·3 per cent carbon, 3 per cent nickel steel consists in heating to 840° C., soaking for a time depending on the mass; and if much machining is necessary the steel is allowed to cool in the furnace until black hot. For normalizing, the materials are heated to 840° C. and cooled in air. This treatment brings the material into the best possible condition for subsequent heat-treatment, and normalizing after machining is therefore advisable.

The properties of some commercial nickel steels are given in the following table; nickel case-hardening steels will be considered later.

C.	Mn.	Ni.	Treatment.	Y.P.	M.S.	Elongation.	Reduction of Area.	Impact.
0·24	0·79	2·60	Normalized 860° C.	21	35	34	36	37
			O.Q. 850° C.: Td. 600° C.	31	43	50	57	59
0·31	0·58	3·22	Normalized 840° C.	24	41	23	40	35
			O.Q. 835° C.: Td. 600° C.	43	53	22	56	61
0·35	0·54	3·64	Normalized 840° C.	28	47	18	39	26
			O.Q. 830° C.: Td. 600° C.	50	61	19	61	63
0·40	0·62	1·10	Normalized 830° C.	24	36	30	41	35
			O.Q. 825° C.: Td. 550° C.	34	44	26	55	33

The effects of tempering on oil-quenched specimens is well illustrated by the following figures, due to Jones: *

Composition of steel: C, 0·38; Mn, 0·43; Ni, 3·97.

All specimens oil-quenched from 850° C.: tempered for 2 hours at the temperatures shown and then air-cooled:

Tempering Temperatures.	E.L.	Y.P.	M.S.	Yield Ratio.	Elongation.	Reduction of Area.	Brinell No.	Impact
—	12	35·6	58·6	·52	11	28	279	16
200° C.	19	37·6	58·2	·65	13	39	271	21
300° C.	25	36·0	56·0	·64	17	41	259	27
400° C.	26	35·7	54·0	·66	19	46	250	29
450° C.	32	37·6	53·7	·70	21	46	250	32
500° C.	33	36·8	52·2	·70	24	55	243	37
550° C.	31	34·9	49·2	·71	24	57	229	51
600° C.	29	34·1	46·6	·73	24	58	218	54
630° C.	29	32·9	45·0	·73	29	62	208	55

It will be noticed that the best all-round properties are not obtained until a tempering temperature of about 550° C. is employed, and the general tempering temperatures for nickel steels are from 550° to 650° C.

* *J.I.S.I.*, 1928 (i).

The manganese content of the above steel is rather lower than is desirable in a plain nickel steel; and Jones has also shown that this element exerts a powerful influence in minimizing the effects of mass on the mechanical properties.

Nickel-chrome Steels.

These are the most important alloy steels for general engineering purposes, since by varied heat-treatments an enormous range of mechanical properties may be obtained, steels of similar composition being employed for very different purposes.

The introduction of chromium results in improved strength and resistance to abrasion, although the characteristic properties of the nickel steels—high tenacity, ductility, and resistance to shock—are still retained. Further, the disadvantages associated with the use of either element separately are almost completely overcome when a suitable combination of both of them is employed. Thus, although chromium tends to promote grain growth in the heat-treated specimens, this action is inhibited by the presence of the nickel. On the other hand, chromium counteracts the tendency of the nickel to induce graphitization of the iron carbide in the steel; a lower manganese content (0·35–0·55 per cent) than that of a plain nickel steel can therefore be employed.

Many nickel-chrome steels are used for drop-forgings and stampings, and for such purposes some consideration must be given to their chemical composition. Thus steels containing:

0·35 per cent C, 1·0 Cr, and 1·0–2·0 per cent Ni forge and stamp well;
0·35   ,,   ,,   1·0 ,, ,,   3·0   ,,   ,,   forge well but stamp badly;
0·35   ,,   ,,   1·5 ,, ,,   3·0   ,,   ,,   are difficult to work.

Chromium influences the air-hardening properties of nickel steels to a very marked extent, but this influence is also dependent on the nickel content. Thus, whilst steels containing 1 per cent chromium and 3 per cent nickel may exhibit very pronounced air-hardening properties, those containing the same amount of chromium but between 1 and 2 per cent of nickel do not air-harden to any appreciable extent.

Nickel-chrome steels of different compositions may be used for similar purposes, the desired properties being obtained by different heat-treatment. Steels containing 0·25–0·4 per cent carbon, 2·5–3·5 per cent nickel, and up to 1 per cent chromium are extensively employed, and these steels are often supplied to the engineer in the heat-treated (oil-quenched and fully tempered)

condition. In this state, the tensile strengths are from 50 to 65 tons per square inch, but the steels machine well and will take fine threads. After machining, the articles are placed into service without further heat-treatment, for such purposes as crankshafts, axles, &c.

Typical heating and cooling curves are given in fig. 102, and if these curves are compared with those given on p. 127 for a plain nickel steel, the effect of the chromium in raising the Ac point and in bringing about a further depression of the Ar point will be readily observed. In a steel containing 0·3 per cent carbon, the Ac point is lowered by about 10° C. for each 1 per cent nickel addition, as against an increase of about 15° C. for each 1 per cent chromium. The net effect, when taken in conjunction with the somewhat lower manganese content, is a slight raising of the critical ranges as compared with those of the plain nickel steels. The heat-treatment temperatures, however, do not differ very much from those of the chromium-free steels, in view of the combined obstructing influences of the nickel and chromium on the structural transformations in the steel, whereby the wholly martensitic state is readily obtained. A mild form of quenching may be employed, such as quenching in oil, or in some cases by simply cooling in air; and such treatment greatly lessens the liabilities to cracking and distortion.

Some typical compositions are given in the following table, together with the treatments generally adopted:

C.	Cr.	Ni.	Treatments.	Uses.
0·35	0·5	1·0	Normalized 880°–900° C.	
			O.Q. 850° C.: Td. 650°–680° C.	Crankshafts, axles, connecting-rods, valve-guides, &c.
0·35	1·0	2·0	N. 830°–850° C.	
			O.Q. 825° C.: Td. 600°–650° C.	Bars for machining, bolts, studs.
			O.Q. 825° C.: Td. 500° C.	Connecting - rods, crankshafts.
0·30	1·0	3·0	N. 810°–830° C., and reheat to 650° C. and air-cool for machining.	
			O.Q. 810° C.: Td. 650° C.	Connecting - rods, axles, cranks.
			O.Q. 810° C.: Td. 220°–250° C.	Gears for hard wear.
0·35	0·7	3·5	N. 820°–840° C., and reheat to 650° C. and air-cool for machining.	
			O.Q. 820° C.: Td. 650° C.	Bars for machining, connecting-rods, crankshafts, &c.

The effects of tempering on the properties of a typical nickel-chrome steel are represented graphically in fig. 103, and it will be observed that a decided minimum in the impact curve occurs at about 350° C. This is typical of many Ni-Cr steels, although the tempering temperature corresponding to this minimum is somewhat dependent on the composition of the steel. In some cases, the impact curve rises very sharply on either side of the minimum, but in others the curve flattens out and the steel then has a low resistance to shock after tempering at any temperature within a certain range. Nickel-chrome steels are therefore not generally tempered in the range 250°–400° C.

Even when a higher tempering temperature is employed, low impact values are obtained if the steel is allowed to cool slowly throughout the above temperature range; but if it is quenched in oil or water from a higher tempering temperature, much better results are obtained. This phenomenon is known as *temper-brittleness*, and is only revealed by the impact test, as is shown by the following data, due to Greaves, Fell, and Hadfield: *

Fig. 102.—Inverse-rate Curves of a Nickel-chrome Steel containing Carbon, 0·33 per cent; Manganese, 0·67 per cent; Chromium, 0·87 per cent; Nickel, 3·35 per cent.

Composition of steel: C, 0·26; Si, 0·07; Mn, 0·66; S, 0·02; P, 0·026; Cr, 0·84; Ni, 3·53.

Treatment.	E.L.	Y.P.	M.S.	Elongation.	Reduction of Area.	Brinell No.	Impact, ft.-lb.
Oil-hardened 850° C. and then cooled in furnace from 650° C.	33	38·4	48·2	22·5	56	237	8
Oil-hardened 850° C., tempered at 650° C. and quenched in water.	31	38·8	48·7	21·0	56	240	59

In industrial practice, quenching in water from 500° to 600° C. may give rise to the production of serious internal stresses; consequently the less drastic method of quenching in oil is generally employed after tempering. The true cause of temper-brittleness has not yet been established, and no indication is given by the microstructure. It has been attributed to high phosphorus in the steel, but the phenomenon has also been found to occur in electric
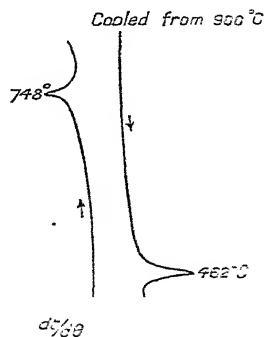
furnace steels of exceptionally low phosphorus content. Andrew and Dickie * conclude that it is due to carbide segregation at the grain boundaries, although this is not revealed under the microscope even at very high magnifications. In several steels recently examined by the author, those showing the most pronounced dendritic structure when etched with Oberhoffer's reagent gave the lowest impact values.
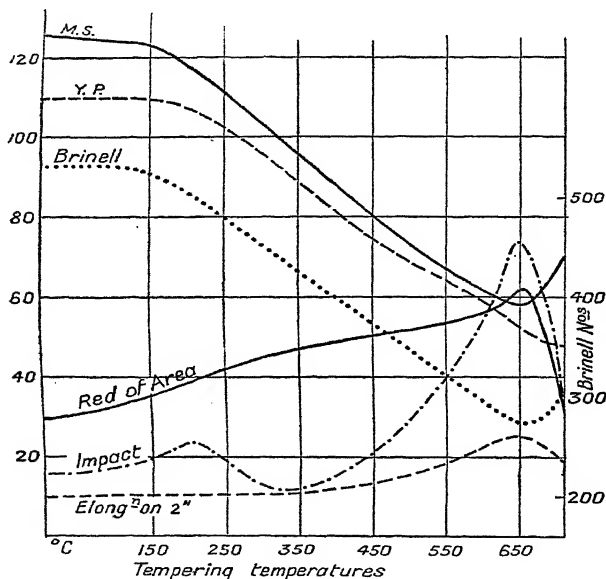

Fig. 103.—Curves showing Mechanical Properties of Nickel-chrome Steel (C, 0·35; Mn, 0·5; Cr, 0·6; Ni, 3·25) after oil-quenching from 820° C. and tempering at various temperatures. Each specimen treated in bars (16″ × 1¼″ diam.) and quenched in oil after being tempered.

Brearley considers that temper-brittleness most commonly occurs in Siemens open-hearth steels, less often in electric steels, and never in crucible steels. Manganese above 0·5 per cent appears to increase the susceptibility to temper-brittleness, and this must be considered when a higher manganese content is employed to counteract the effect of mass in large sections.

The introduction of 0·3–0·5 per cent of molybdenum appears to reduce the susceptibility to temper-brittleness to an almost negligible extent, but quenching in oil from the tempering temperature is always advisable, even in steels containing this element.

Of the lower nickel Ni-Cr steels, that known as K.E. " 805 " merits special mention, since it has earned a remarkable reputa-
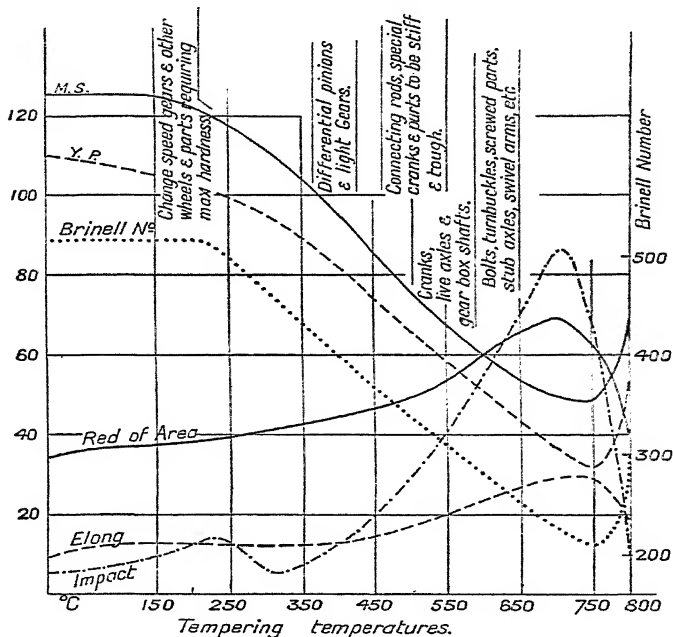

Fig. 104.—Size of pieces treated, 16″ × 1¼″ round. All pieces oil-quenched from 820° C. and quenched in oil from tempering temperatures

tion in the automobile industry, which is not surprising in view of the enormous range of properties which can be obtained from it by varied heat-treatments. This steel has approximately the following composition:

C, 0·35; Si, 0·35; Mn, 0·4; Cr, 1; Ni, 1·25; Mo, 0·3.

The effects of tempering on the oil-hardened specimens are shown in fig. 104, and the purposes for which the material is suit-

able after tempering in specified temperature ranges are indicated on the diagram.   When tempered at 550°–650° C., the following test results are obtained:

| M.S.	Elonga-tion.	Reduction of Area.	Brinell No.	Impact.
55–70	15–22	44–60	255–321	40–70

In this condition the material is readily machined, and is used for cams, couplings, clutches, die-blocks, trip-gear, links, loco-crank pins, keys, thrust blocks, crane and turbine shafts, &c.

A steel containing 0·65 per cent carbon, 0·7 per cent chromium, and 1·25 per cent nickel has been used with great success for stamping dies.   After oil-hardening at 860° C. and tempering at 500°–550° C., this steel has a tensile strength of 85 tons per square inch with impact figures of 40–50 ft.-lb.

Microstructures of heat-treated nickel-chrome steels do not, in general, lend themselves to such ready interpretation as those of carbon steels, and, moreover, steels of greatly different composition but in different conditions of heat-treatment may exhibit similar structures.   Some knowledge of the chemical composition is therefore essential before any definite opinion can be expressed as to the true condition of a heat-treated nickel-chrome steel, and in many cases the desired information can only be obtained satisfactorily by comparing the structure with a series of standard microstructures of a steel of similar composition, the treatments and properties of which are known.

The microstructures of small heat-treated specimens of a typical nickel-chrome steel are given in fig. 105, and it will be observed that the normalized specimen is decidedly martensitic. The steel is, in consequence, much too hard for machining, and if a nickel-chrome steel is to be machined, it must either be annealed or reheated to about 600° C.   The latter treatment, which is in reality a tempering operation to break down any martensite formed as a result of previous treatment, is to be preferred when the articles have to take fine threads.   On the other hand, if much machining is necessary, the steel must be annealed in order that a heavy cut may be employed.

The acicular nature of the martensite in a quenched nickel-chrome steel is generally well defined, and this aspect often persists in the fully tempered specimens.   The sorbite in many quenched and fully tempered specimens thus has a distinctly martensitic appearance, and if the steels are not etched very care-
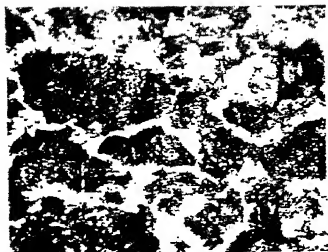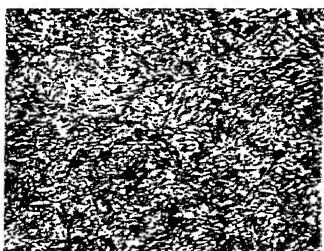
(a) Annealed 825° C. Vickers
diamond hardness 240

(b) Oil-quenched 830° C. Vickers
hardness 657
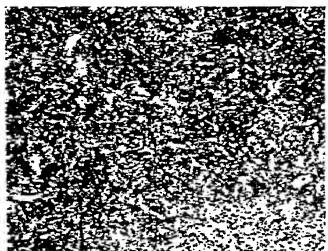
(c) O.Q. 830° C. Tempered 600° C.
Vickers hardness 317

(d) Normalized 825° C. Vickers
hardness 527

Fig. 105.—Microstructures of small heat-treated specimens of Ni-Cr steel:
C, 0·35; Cr, 0·6; Ni, 3·25. × 375

Fig. 106.—Quenched and tempered
nickel-chrome steel. × 375

Acicular nature of sorbite suggests an initial quenching
temperature much too high

fully, it is difficult to distinguish one constituent from the other at comparatively low magnifications. The small carbide particles in the sorbite can, however, generally be observed at higher magnifications.

The martensitic character of the sorbite may be taken as an indication of the temperature from which the steel has been quenched before being tempered. A high quenching temperature yields a coarse martensite, which in turn gives rise to the formation of a sorbite exhibiting a coarse martensitic appearance, as shown in fig. 106. Such structures yield low impact figures. When higher tempering temperatures are employed, coalescence of the carbide particles takes place, and the martensitic aspect of the sorbite more or less disappears. These changes, however, are accompanied by a very rapid falling off in the strength of the steel.

Air-hardening Nickel-chrome Steels.

These steels are essentially martensitic when cooled in air from about 830° to 840° C., and can therefore be hardened with a minimum amount of distortion. For this reason machining of the unhardened material can be carried out within very close limits, a small allowance for final grinding being made.

Typical compositions and mechanical tests on the air-hardened bars are as follows:

C.	Cr.	Ni.	M.S.	Elongation.	Reduction of Area.	Brinell No.	Impact.
0·30–0·35	1·25–1·5	4·5	115–120	10–12	30–40	418–512	20–30

Typical heating and cooling curves are given in fig. 107, and the great depression of the Ar point, upon which the air-hardening properties depend, will be observed. In this respect, however, the influence of initial temperature must be considered, as will be evident from the curves. Forgings and drop-stampings are much too hard for machining, but after normalizing at about 810° C. and reheating to 650°–700° C., the steels are softened somewhat and are readily machined if good quality tools are employed. For gears, pins, and small shafts to withstand hard wear, the steels are either oil-quenched or air-cooled from about 830° C. and tempered at 150°–250° C. A higher temperature (550°–650° C.) is employed for connecting-rods and other parts where great strength and resistance to abrasion are desired. Air-hardening steels of this type are characterized by their uniformity in structure and properties, and the effects of mass are therefore almost negligible

Comparatively large masses can be treated so as to yield identical tests with those obtained from much smaller sections. The microstructure of an air-hardened nickel-chrome steel is shown in fig. 108 (facing p. 146). The advantages associated with the use of air-hardening steels will be readily appreciated. At the same time, however, the materials must be cooled fairly slowly and uniformly after forging, otherwise there is the possibility of the development of minute surface cracks, the deleterious effects of which become more pronounced during any subsequent heat-treatment.
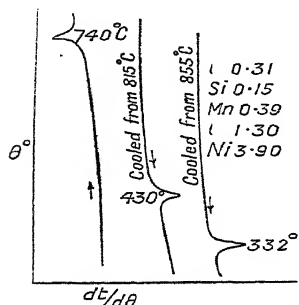
Fig. 107.—Inverse-rate Curves for a typical "Air-hardening" Nickel-chrome Steel, showing effect of initial temperature on its critical point.

Another interesting Ni-Cr-Mo steel of the air-hardening type contains 0·5 per cent C, 0·5 per cent Cr, 4·5 per cent Ni, and 1·25 per cent Mo. This steel is used for extrusion rams and dies. Normalizing is carried out at about 850° C., but the steel is not machinable in this state. It is therefore reheated to about 675° C. and cooled in air.

The influence of small quantities of molybdenum in reducing the susceptibility to temper-brittleness of the nickel-chrome steels has already been mentioned, but the element also apparently confers a resistance to oxidation, and thus improves the heat-resisting properties of Ni-Cr steels which are used at higher temperatures, such as those used for the dies in drop-forging.

Austenitic Nickel Steels.

Steels containing from 20 to 35 per cent nickel cannot be heat-treated like the lower nickel steels, and are entirely austenitic even when slowly cooled. Machining is not easy but is possible, particularly after they have been heated to 800° C. and cooled in air. These steels are non-magnetic, exceedingly tough, and have a low coefficient of expansion. They are also very resistant to corrosion by sea-water, and have found considerable application in marine engineering, although they are now being superseded by the high-chromium "stainless" steels. Typical compositions and applications are as follows:

C.	Mn.	Cr.	Ni.	Uses.
0·45–0·50	1·25–1·50	0·50	30·0	Turbine blades, gas-engine valves, magneto-spindles, &c.

The high manganese and the chromium are necessary to prevent graphitization of the carbide of iron during working.

Tungsten Steels.

Tungsten is extensively employed in tool-steel manufacture. Comparatively small quantities impart a very fine grain to the steels, which are just as hard but less brittle after hardening than plain carbon steels used for similar purposes. Tungsten steels are also affected to a much lesser degree by incorrect heat-treatment, there is less tendency towards decarburization during working, and the carbides are rendered much more stable; consequently, taps, dies, turning tools, &c., are greatly improved by even very small additions of the element.

In the presence of sufficient carbon, practically the whole of the tungsten exists as the very simple stable carbide WC, although in higher tungsten steels of the high-speed type there is definite evidence of the formation of a very hard tungstide of iron Fe_3W_2.

Tungsten raises the critical points in steel, and solution of the carbide occurs over a range of temperature at a comparatively slow rate. When complete solution has been obtained, however, the reverse transformations on cooling are rendered so sluggish that the steels exhibit very pronounced air-hardening properties. Up to 2 per cent tungsten, the annealing temperatures are about 780°–800° C., whilst the hardening temperatures are about 20°–30° C. above those for the corresponding carbon steels. When a hardened tungsten steel is reheated, the martensite breaks down, but at higher temperatures than in carbon steels. Consequently, tungsten tool steels are particularly suitable for heavy machining where the nose of the tool is subject to a considerable rise in temperature.

Steels containing about 2 per cent carbon and 5–10 per cent tungsten are used for wire-drawing dies. These resist abrasion to a very remarkable extent, but are somewhat difficult to machine. Although a critical point occurs at about 760° C. on heating, these steels must be heated to about 950°–1000° C. if they are to be hardened effectively. When air-cooled from such temperatures, the air-hardening properties are so pronounced that the steels are fully hardened.

Steels containing 0·65–0·7 per cent carbon and 6 per cent

tungsten are extensively employed for permanent magnets, but the best properties are only obtained when the steel is in the fully hardened (martensitic) condition, as will be evident from the following data due to Crapper:

	H_c.*	B_r.*	$B-H_{max}$.*
Annealed:	26	11313	128,800
Hardened:	73	10684	308,000

The usual treatments for a tungsten magnet steel consist in annealing at 780°–800° C., and after machining the magnets are hardened in oil from about 850° C. It has been shown by Evershed † that the prolonged annealing of a tungsten steel results in a lowering of the value for the coercive force after hardening, but the steel can be restored by reheating to about 1250° C. for a few minutes, cooling in air, and then rehardening in oil or water.

Some typical analyses of tungsten steels are given below; others are considered with the high-speed and heat-resisting steels.

C.	Mn.	W.	Cr.	Uses.
1·05	0·40	0·50		Dies.
0·45	0·25	0·60		Springs.
1·05	0·35	1·00		Taps. Water-hardening
1·20	0·40	2·00		Taps. Oil-hardening.
0·65	0·40	6·00	0·50	Permanent magnets.
2·00	0·70	5·0–10·0		Drawing dies.

Cobalt Steels.

Cobalt, when added to steels containing about 0·9 per cent carbon, improves the magnetic properties for permanent magnets, and the high cobalt steels are greatly superior to the usual tungsten magnet steels.   Cobalt may confer increased remanence, but the

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* The two constants, remanence (B_r) and coercive force (H_c), are generally used to denote the properties of a permanent magnet steel. The remanence is the flux-density in the magnet when the magnetizing force has been removed, whilst the coercive force represents the magnitude of the negative magnetizing force which must be applied to demagnetize the magnet. These values are indicated by the points at which the descending portion of the hysteresis loop crosses the B and H axes. If the corresponding values of B and H for points on the portion of the curve intercepted by the two axes are multiplied together, a series of energy products is obtained which when plotted against the flux-density B as shown on p. 139 indicate a maximum B–H value. This method of plotting is due to Evershed, and the maximum ($B-H_{max}$.) is a most important criterion of the properties of a permanent magnet steel, since it not only serves as a means of comparison of the relative qualities of different magnet steels, but is also of value in determining the volume of steel required for a magnet designed for a specific purpose. Typical values of B–H_{max}. for carbon (0·9 per cent carbon), chromium, and tungsten magnet steels are 200,000 240,000, and 280,000–300,000 respectively.

† *J. Inst. Elect. Eng.*, 1925, Vol. LXIII.   See also Swann, *J.I.S.I.*, 1928 (i).

most striking effect is the remarkable increase in the value for the coercive force, and this yields a much higher $B-H_{max}$ value, as will be evident from fig. 109. Cobalt metal is costly, however, and the high cobalt steels are extremely hard and brittle, and require such extreme care in forging that a certain amount of chromium is often substituted for cobalt. The chromium also serves to prevent carbide decomposition during hot-working and annealing.
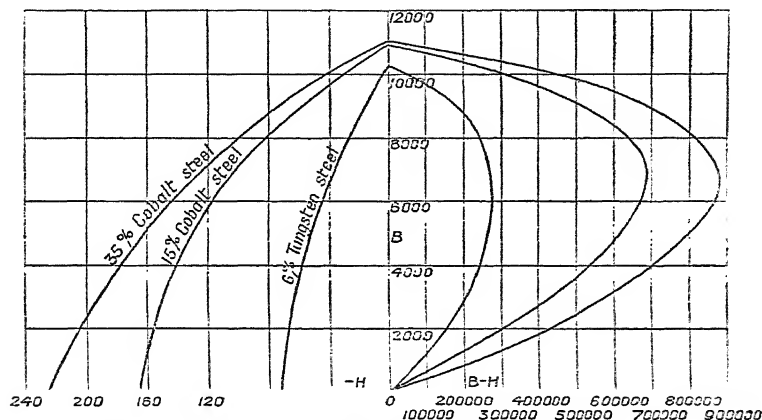

Fig. 109.—B-H and B-BH Curves for Tungsten and Cobalt Magnet Steels

Typical analyses of such steels are as follows:

C.	Mn.	Cr.	Co.	Mo.
0·9	0·4	9·0	6·0	0·5
1·0	0·4	9·0	15·0	1·0

The full investigation of the influence of cobalt on the properties of magnet steels is due to Honda, whose well-known K.S. steels vary between the following limits:

C.	Cr.	W.	Co.
0·4–0·8	1·5–3·0	5·0–9·0	30·0–40·0

The following treatments are recommended for 6, 9, and 15 per cent cobalt magnet steels:

Forging: between 950° and 1100° C.
Annealing: between 700° and 720° C.
Hardening: (i) heat to 1150° C. and cool in air, (ii) after standing for several hours reheat to 700° C. and again air-cool, and finally (iii) reheat to 970°–1000° C., cool in air blast until black-hot and then quench in oil.

Note on the Magnetization of Permanent Magnets.—Magnetization is carried out by placing the magnets in a magnetic field of sufficient strength. The length of time that the magnets remain in this field does not appear to have any pronounced influence, but the intensity of the magnetizing field is of the utmost importance, as will be observed from the following figures, due to Crapper, for a tungsten steel:

H_{max}	95	130	165	210	250	C.G.S. units	
H_c	59·4	69	74	75	75	,,	,,
B_r	4800	7600	8400	9200	9200		

Thus in order to obtain the maximum efficiency from a magnet, the magnetizing force must be sufficient to saturate the steel. A field strength of at least 400 gausses is recommended for tungsten steel, but a field of 1500 gausses is required for cobalt steel magnets.

Rough handling and vibrations in transit may seriously impair the properties of a finished magnet, and it is therefore always advisable to remagnetize the steel immediately before use.

Cobalt-chromium steels are also used for tools, but in view of their relatively high cost, to a limited extent only.

Cobalt is also a constituent of many " super " high-speed steels used for particularly heavy work.

Silicon Steels.

This element readily alloys with iron and is sometimes intentionally introduced into steel. The silicon forms a silicide of iron FeSi, and in the solid steel this exists in solid solution in the ferrite. These effects are shown in fig. 110, and the closed curve showing the limits of existence of γ iron will be readily observed, a fact which lends further support to the view that α and δ iron are identical.

Silico-manganese steels are commonly employed for springs, the compositions varying between the following limits:

C, 0·5–0·6; Si, 1·25–2; Mn, 0·6–0·9.

Silicon raises the critical points, and these steels must therefore be heated to higher temperatures for hardening than the corresponding plain carbon steels. The springs are generally oil-quenched from 875°–900° C., and when tempered at 475°–525° C. give Brinell numbers of about 415–444. In this condition, sorbitic

structures obtain, and the steels are characterized by their toughness and resistance to fatigue, particularly at higher temperatures. Silicon steels are rather susceptible to grain growth, however, and the heat-treatment must be carefully carried out if the best results are to be obtained.

Almost carbonless alloys of iron and silicon were first evolved by Sir R. Hadfield for use in electrical machinery, where a material having a low hysteresis is desired. These alloys may contain up to 4 per cent silicon, and the following composition is quite typical:

C, 0·05; Si, 3·4; Mn, 0·32; S, 0·04; P, 0·01.

The high silicon tends to decompose any carbide of iron present, and since this element also increases the electrical resistance of the iron, eddy current losses are reduced to a minimum when the material is used for the laminated cores of transformers. Manganese hinders carbide decomposition and thus tends to increase the hysteresis losses, but a small amount is necessary as an insurance against dissolved oxide of iron. The usual treatment consists in cooling very slowly after thoroughly soaking at about 900° C. Cold-work adversely affects the magnetic properties, and the annealed sheets should therefore be subjected to as little strain as possible.

Fig. 110.—Part of Equilibrium Diagram: Iron Silicon Alloys

These steels are mainly used for transformers; for dynamos soft iron is still preferred.

Manganese Steels.

Manganese, in small amounts, is an essential constituent of almost any steel, but such small quantities do not greatly affect the properties of the materials. Some of the higher manganese steels possess characteristic properties which render them particularly suitable for certain specific purposes. The lower-carbon high-manganese steels have not been widely employed owing to
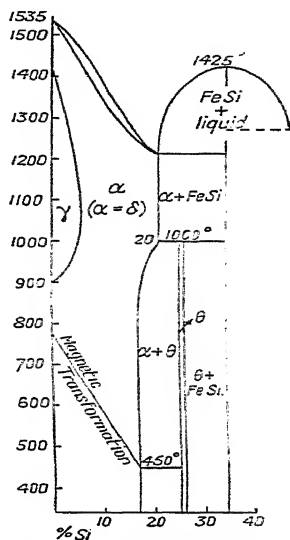
the popular impression that such materials are brittle. This brittleness may, however, have been almost entirely due to incorrect treatment; and there is little doubt further research will show that such steels, when properly made and treated, can be used to replace some of the more expensive alloy steels for many engineering purposes.

The constitutions of the slowly cooled manganese steels are indicated in the diagram (fig. 111), due to Guillet. Of the normally pearlitic steels, those containing 1–2 per cent manganese are the most important. Steels containing this amount of manganese and 0·25–0·5 per cent carbon are used for such purposes as dredger-buckets, &c., where toughness and resistance to abrasion are required. Such articles are generally heat-treated after being cast to shape. In U.S.A., mild steels containing about 1·5 per cent manganese are extensively used as free-cutting steels.
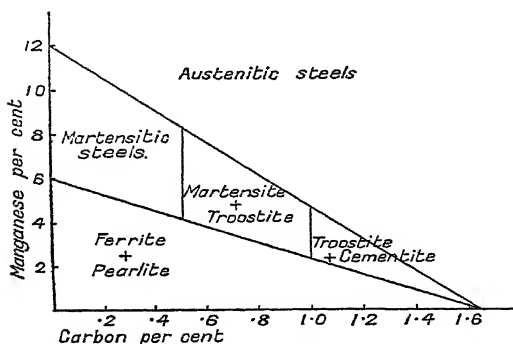
Fig 111.—Showing Effect of Manganese on the Constituents of Annealed Steels

"Non-shrinking" tool steels containing about 0·8–0·9 per cent carbon and 1–2 per cent manganese are employed for those purposes where extreme accuracy of size and shape after heat-treatment is essential. Heat-treatment generally consists in normalizing from 770° C. and then hardening in oil from 790°–800° C., a mild tempering being given to suit requirements. Owing to the more or less complete suppression of the volume changes which normally occur during slow cooling, the volume of an ordinary carbon steel is altered by quenching, but the size of a high manganese tool steel is affected to a much less extent. In addition, the milder form of quenching employed, and the peculiar properties of the steel itself, reduce warping to an absolute minimum. A steel of this description is therefore suitable for precision tools, taps, reamers, drawing and redrawing dies, milling cutters, gauges, &c. If much machining is necessary, the

steel is annealed by heating to 800° C. and cooled very slowly in the furnace.

The most important of the steels of very high manganese contents are those evolved by Sir R. Hadfield, containing 1–1·25 per cent carbon, 0·25–0·4 per cent silicon, and 12–13 per cent manganese.   A steel of such a composition is generally known as " manganese steel ", and possesses some very peculiar properties. As will be evident from Guillet's diagram, this steel is essentially austenitic under ordinary conditions. The austenite is completely retained by quenching from 1000° C., the iron then being in the γ condition. A plain carbon steel of the same carbon content after similar treatment would be very hard and brittle, but this manganese steel is in its softest condition. The Brinell hardness number is only about 200, and the steel is easily dented by a hammer and chisel, but the chisel will not cut it and the material cannot be filed. Consequently, it is generally supposed to be unmachinable. The steel can, however, be drilled, turned, or shaped by some of the " super " high-speed steels which have been developed comparatively recently. The material will forge at a high temperature, and manganese steel is therefore generally used in the forms of castings or forgings, any final shaping being brought about by grinding on emery. The steel is obtained in the best condition for working and grinding by quenching.   The following test results for a steel containing 1·1 per cent carbon and 12 per cent manganese are typical:

Condition.	M.S.	Elastic Limit.	Elongation
Cast	36	20	30
Rolled	62	29	30–40
Forged	63	25	38
Annealed	46	28	3
Quenched 1000° C.	55	—	40

Annealing thus makes the material very brittle. If the quenched steel is tempered, it changes over to martensite, and martensite is also obtained by cooling it in liquid air. The Brinell hardness of the martensite is much greater than that of the austenite, but the ductility practically disappears.   The austenitic steels are non-magnetic in view of the fact that the iron is in the γ condition, and magnetism only appears when some of the iron changes to the α form. These effects are illustrated by the following data:

Condition of Steel.	Brinell No.	Properties.
W.Q. 1000° C.	200	Non - magnetic and tough.
Td. 3 weeks at 300° C.	217	Non-magnetic but less tough.
Td. 3 hours at 400° C.	322	Magnetism 0·12 per cent of pure iron, steel somewhat brittle.
Td. 3 hours at 530° C.	400	Magnetism 24 per cent of iron and steel very brittle.
Qd. from 760° C.	277	Magnetism 0·3 per cent of pure iron.

All these changes are due to the austenite-martensite transformation, martensite being brittle and magnetic due to its α iron. The change is not brought about at a rapid rate by ordinary thermal treatments, but a very rapid conversion is obtained by the application of cold-work. An austenitic steel with a Brinell number of only 200 would be expected to file easily, but immediately the file is applied the surface is converted into glass-hard martensite. For this reason, manganese steel exhibits extraordinary wearing properties, owing to the facility with which the surface changes to martensite, the underlying material, however, still being retained in the tough condition.

Manganese steel is used for containers in rock-crushing machines, tramway and railway crossings, and railway rails where wear is heavy, as on bends. Rails are rolled in ordinary rail mills, but after the last pass, are plunged in water. The life of manganese steel rails used on sharp bends with very heavy traffic is given as 9 years, as against about 9 months for ordinary carbon steel rails.

Dredging buckets are also made of manganese steel, objects of this kind being generally cast to shape, then heated to 1000° C. and quenched in water. These steels are used for bullet-proof helmets, since the material is very resistant to penetration, and does not shatter.

In the very toughest condition, the maximum stress is about 55–60 tons per square inch, with 40 per cent elongation; and in this condition machining is possible, although ordinary tools wear out very quickly. In machining, the tool must actually cut and not rub the surface, otherwise the formation of an extremely hard surface layer is obtained. A very sharp tool should therefore be

employed, and it must be reground immediately the cutting edge has gone.

Annealing is never applied to this steel, as the material is then so very brittle. Incorrect treatment may lead to the formation of free carbide at the grain boundaries, and the steel is then brittle and almost unmachinable.

Molybdenum and Vanadium Steels.

Molybdenum apparently has a similar effect to that of tungsten on steel, but in a more marked degree, 1 per cent of the element being as effective as about 2·5 per cent tungsten.

The influence of small amounts of molybdenum in reducing the susceptibility of heat-treated nickel and nickel-chrome steels to temper-brittleness has already been mentioned, as also its use as a constituent of steels used for extrusion rams and dies.

Small quantities of molybdenum yield a finer " grain ", and improve the properties of many of the heat-resisting alloys. Nickel-chrome steels containing small amounts of molybdenum, used for such purposes as dies in drop-forging, do not scale so readily and have a longer life than those free from molybdenum.

This element is also a constituent of some of the " super high-speed " steels; and tool steels containing about 0·9 per cent carbon, 3–3·75 per cent chromium, and 3–3·75 per cent molybdenum are manufactured in fair quantities.

Molybdenum is introduced into these steels as ferro-molybdenum or as molybdenum powder. Both these materials are made from the sulphide (MoS_2) ores which are roasted to the oxide before extraction of the metal, and the quantity of sulphur in the product obviously depends on the extent to which the roasting process is carried out. Certain cases have arisen in which a disastrous sulphur content has resulted in the steel.

Vanadium is a valuable metal for ensuring soundness in steel ingots, and as a scavenger for oxides it has probably no superior. Small amounts (0·1–0·2 per cent) are often added for this purpose alone to tool steels, chrome, and chrome-nickel steels.

Higher vanadium steels are usually those of the high-speed type. The element is added as ferro-vanadium, generally made by the " Thermit " process, and may contain appreciable amounts of silicon and aluminium. Phosphorus is also a probable impurity, and may be present to such an extent as to exert a harmful influence on the properties of high vanadium steels.

Tool Steels and their Treatment. High-speed Steels.

Tool steels generally contain more carbon than structural steels, and since hardness is of primary importance, the final structures are almost entirely martensitic.

Silicon, sulphur, and phosphorus should be as low as possible, and the manganese content of a tool steel is of great importance. High carbon steels for water-quenching should not contain more than 0·35–0·4 per cent of manganese, although oil-quenching steels may contain as much as 0·55 per cent. The steels of the higher manganese content tend to crack when quenched in water, but oil-quenching can be safely carried out upon them without risk of cracking or lack of hardness.

Typical compositions of plain carbon tool steels are given in the following table:

C.	Purposes for which Suitable.	Remarks as to Welding.
1·40 per cent.	Saw-files, razors, brass-working tools, drawing dies, roll-turner's tools, &c.	Will not weld.
1·35–1·25 ,,	Turning, slotting, and planing tools, small cutters, &c.	Will not weld.
1·15 ,	Drills, cutters, reamers, small taps, dies, punches, &c.	Will weld with great care.
1·05 ,	Taps, large reamers, ball-races, wood-working tools, &c.	Will weld with care.
0·85 ,	Cold chisels, hot setts, small shear blades, stamping and pressing dies, heavy screwing dies, &c.	Will weld without difficulty.
0·75 –0·65	Cold setts, miner's drills, smith's tools, hammers, stamping and pressing tools, set screws, hot impact work in general, and for general welding purposes.	Readily welded.

Bearing in mind the effect of the manganese on the eutectoid ratio, it is evident that many tool steels contain excess cementite, which in the cast state exists as a network around the pearlite grains. The cellular pattern must be destroyed before the tools are hardened, otherwise they tend to crack during the quenching process. The ideal structure of a high carbon steel ready for hardening consists of small rounded particles of cementite in a matrix of finely laminated pearlite, and this structure can only be obtained by a combination of correct mechanical and thermal treatment. The forging temperatures are generally below 1000° C., and the steel should be worked throughout the critical range, since if work is ceased at too high a temperature, the cementite
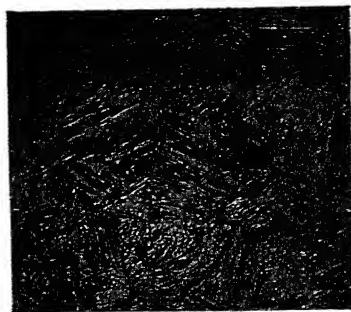
Fig. 108.—Microstructure of air-hardened
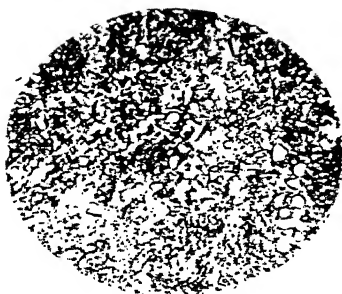nickel-chrome steel. × 375

Fig. 112.—1·4 per cent C steel, worked
and annealed. Globular cementite in
pearlite matrix. The pearlite shows some
tendency towards divorcement, but the
general structure is good. × 375.

Fig. 113.—Hardened 1·4 per cent steel
in ideal condition: globules of excess
cementite in martensite matrix. The
etching was not sufficiently prolonged to
reveal the structure of the martensite, but
the troostite borders around the carbide
globules are readily observed. × 300.

Fig. 114.—Internal hardening cracks in drastically
overheated tool-steel. × 200

subsequently deposited will again exist as cell walls around the pearlite. If work is continued until the temperature of the steel is only just above the Ar_1 point, the particles of cementite are dispersed throughout the mass as they are deposited from the austenite, and the possibility of the formation of a cellular structure is thereby lessened. At the same time, however, forging should not be continued much below this temperature, otherwise severe strains are induced, and forging cracks may develop. High carbon steels should always be slowly cooled after forging, and it is advisable to place the forged articles, whilst still hot, into a furnace at about 760°–780° C. and cool them slowly in the furnace.

Annealing is necessary, after forging, in order to obtain the desired structure. The temperatures employed are about 50° C. above the Ar_1 points, as indicated by the line BC on the diagram on p. 101. Most of the excess cementite thus remains undissolved, but under the influence of surface tension forces the carbide particles assume globular forms around which any cementite is deposited on subsequent cooling. The final structure thus consists of isolated spherical particles of the excess cementite in a pearlite matrix (fig. 112), and such materials show little or no tendency to crack when quenched from a correct hardening temperature. The same temperatures are employed for hardening as for annealing, and after quenching the structure thus consists of carbide particles embedded in a background of martensite of about 0·9 per cent carbon strength (fig. 113). The steel is then in its hardest condition.

Most tools are slightly tempered before use. This treatment may decrease the hardness a little, but is necessary to release hardening strains and avoid excessive brittleness. High carbon steels tend to develop belated cracking after hardening, and even in cases where maximum hardness is desirable, it is always advisable to subject the material to a very mild form of tempering, such as heating in an oil-bath at a temperature of about 120°–150° C., or even in boiling water. Such treatment, if carried out immediately after hardening, greatly lessens the liability to cracking, but has no appreciable effect on the hardness.

Higher tempering temperatures are employed in order to obtain the desired toughness in steels used for certain specific purposes. The tempering of tools is often carried out by noting the colour changes which take place on the polished surface of the hardened steel when it is reheated. The colour, which is due to

a very thin film of oxide on the surface, gradually changes from pale yellow to blue as the temperature is raised. The colour developed at a particular temperature is somewhat dependent on the length of time the steel is maintained at this temperature, but if the time is less than half an hour, the following table is sufficiently accurate for most purposes:

Colour.	Temperature.	Articles to which Treatment is Applicable.
Blue	300° C.	Springs, wood-working saws.
Mauve	290° C.	Cold chisels for wrought iron.
Dark purple ..	280° C.	Cold chisels for steel and cast-iron hot setts.
Purple	270° C.	Press tools, flat drills for brass.
Deep brown to purple	260° C.	Twist drills, reamers, punches, dies, cups, snaps.
Brown	250° C.	Taps, shear blades for metals, screw-cutting dies, rock drills.
Golden brown ..	240° C.	Milling cutters, drills.
Deep straw ..	230° C.	Planing and slotting tools.
Medium straw ..	220° C.	Screwing dies for brass, light-turning tools, lathe tools.
Pale straw ..	210° C.	Very light lathe tools for finishing work.

It should be noted that the above temperature-colour relationships apply only to plain carbon steels, and although they may be applied to high carbon tool steels containing less than 5 per cent of tungsten without trouble, an entirely new relationship must be established for each of the different classes of alloy steels containing large proportions of alloying elements. Thus, in the case of a typical stainless steel, a pale straw corresponds with about 270° C., a purple to about 475° C., and a blue to about 525° C.

Tools should be quenched in oil or water after the desired tempering colour has been obtained.

When a tool has to be hardened throughout, it is advisable to quench it " right out ", i.e. it should be kept in the quenching medium until quite cold, and then reheated until the required temper colour is obtained. With larger masses, such as large milling cutters, hardening strains can be reduced by quenching in water until black hot, and then transferring them to an oil bath until quite cold.

In the case of turning tools, planing and slotting tools, chisels, setts, &c., it is only necessary to harden the actual cutting part, the main body of the tool being retained in a comparatively soft tough condition. In such cases, the tool is heated to the hardening temperature, but only the cutting end is plunged in and moved

about in the quenching liquid. When this end is quite cold, it is rapidly cleaned with emery or a soft stone, and the heat from the rest of the tool is allowed to flow back until the required colour is obtained, then the whole tool is quenched right out.

Faults in the Treatment of Tool Steels.

The precautions taken to secure the most desirable structure in high carbon steels by working and annealing have already been mentioned, but it must be realized that this structure is readily destroyed by any subsequent overheating, and a cellular structure again formed. Since at this stage the articles are generally about finished size, further work is impossible, and when they are quenched from the ordinary hardening temperatures there is a grave risk of crack development due to the cementite network present. The risk of cracking is minimized somewhat by heating to a temperature just above the cementite line in order to take all the cementite into solution. When quenched from such a temperature the steel is certainly much more brittle than when it has been correctly treated, and this treatment is simply given as being the lesser of the two evils.

Prolonged heating at temperatures well above the cementite line results in the formation of very large austenite grains, and on quenching a very coarse brittle martensite is produced in which both surface and internal cracks readily develop. In many cases, the cracks can be plainly observed to follow the boundaries of the original austenite crystals. Fig. 114 (facing p. 146) shows one of many internal cracks in an oil-quenched 1·2 per cent carbon steel which had evidently been very drastically overheated. Unfortunately, none of the usual mechanical tests serve to indicate the cutting properties of a hardened tool steel, and the only real test which is of value is associated with actual use in the lathe. The steel to be tested is forged to a standard shape, and is used upon a steel of standard composition. The results obtained are then compared with some arbitrarily fixed standard.

Ordinary Brinell ball tests are almost useless, since in many cases the tool to be tested is harder than the ball itself. The latter then becomes distorted and erroneous hardness numbers are obtained. The diamond hardness tests, such as those carried out in the Vickers, Firth, and Rockwell machines, are of some value in indicating whether the tool has been fully hardened or otherwise, although these tests do not show the effects of overheating

before quenching. The appearance of the fracture of a hardened tool steel is a much more important criterion of its properties. Correctly hardened, a tool steel exhibits a very fine grain, but the grain becomes coarser the higher the quenching temperature. It is extremely difficult to indicate this effect by means of photographs, but those shown in fig. 115 will serve to illustrate the effects of somewhat drastic treatments.

Prolonged annealing at a temperature just below the lower critical point often results in the spheroidization of both eutectoid and hyper-eutectoid cementite (fig. 116). Such structures showing drastically " divorced pearlite " are undesirable in most tool steels, since solution of the eutectoid cementite is then only obtained with the greatest difficulty, and the steel is generally lacking in hardness if quenched from the ordinary hardening temperatures. The steels can only be hardened satisfactorily by heating to a much higher temperature before quenching. Such treatment, however, induces excessive brittleness, and it is then necessary to reharden the material from a correct temperature if a satisfactory product is to be obtained. In certain exceptional cases, spheroidization of the whole of the carbide is rather desirable than otherwise. Thus in files it is imperative that there should be not the slightest trace of any cellular pattern in view of the very drastic method of quenching adopted, namely, by quenching in cold brine water. In such cases, the size and distribution of the particles of excess carbide is the more important factor.

It has already been mentioned that the structure of a correctly hardened tool steel consists essentially of martensite, and if this structure is not obtained, the cutting properties of the tool are seriously impaired. Again, the high carbon steels (with or without chromium) which are used for ball and roller bearings are only in the best condition to resist wear when their structures are almost entirely martensitic, and several failures examined by the author were due to the presence of much troostite in the microstructures. In such instances, the presence of the troostite may indicate: (a) insufficient soaking before quenching; (b) inefficient agitation after the article has been plunged into the quenching medium; or (c) too high a temperature of the quenching fluid, such as may occur when large numbers are being dealt with, and the capacity of the quenching tank is not large enough to absorb the heat of the quenched articles without a considerable rise in temperature.
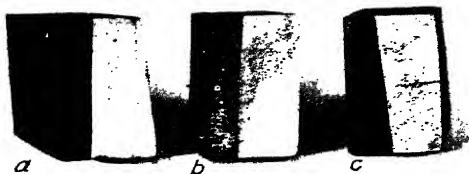
Fig. 115.—Fractures of 1·17 per cent C steel hardened in water at different temperatures: (a) 770° C.; (b) 830° C.; (c) 900° C. Note the crack in (c).
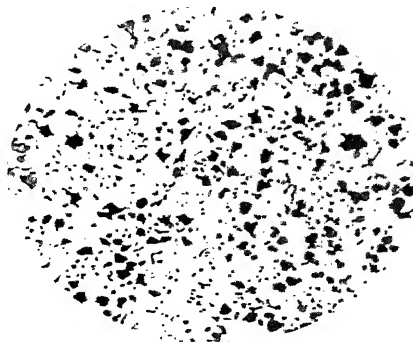

Fig. 116. — Drastically divorced pearlite in 1·1 per cent C steel. The outer layers were heavily decarburized. · 200. Etched with boiling alkaline sodium picrate.
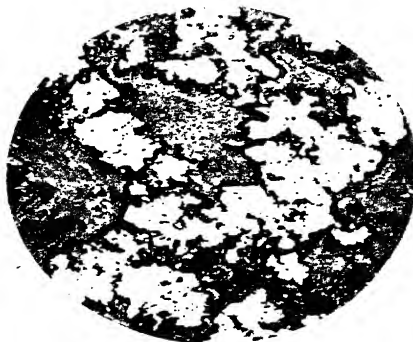

Fig. 117.—0·9 per cent C steel quenched during lower critical change. × 100. Shows martensite (white), troostite (black), and pearlite. Owing to the light etching and the low magnification, the martensitic markings cannot be seen.

In extreme cases, due to (*a*), the pearlite-austenite change may not have been complete when the article was quenched. In such instances, the microstructure consists of martensite together with unchanged pearlite enveloped by troostite (fig. 117). It may be noted that this incomplete lower critical change, either during heating or cooling, is the sole cause of the existence of martensite side by side with pearlite in a quenched specimen. The two constituents occurring together thus afford ample evidence that the steel has been insufficiently soaked or, what almost amounts to the same thing, that too low a quenching temperature has been employed.

High carbon steels are particularly liable to decarburization during heating for hardening, but with careful treatment a grinding allowance of less than $\frac{1}{64}$ in. is all that is necessary, and this should be made wherever possible. Care must be exercised in the grinding of a hardened tool steel, since microscopic surface cracks readily develop, and the failure of many tools by the chipping of cutting edges is often attributable to careless grinding. For this operation, a grindstone, with a plentiful supply of water for cooling, is to be preferred, but a very soft emery wheel may be employed (dry) if a stone is not available. In either case, undue pressure must be avoided, the tool being only lightly pressed against the surface.

High-speed Steels.

R. Mushet discovered the fact that high tungsten steels were extremely hard after simply cooling from the forging temperatures, and the materials thus became known as *self-hardening steels*. When first introduced, self-hard steels revolutionized tool-steel practice, the tools enduring quite well when increased cutting speeds and higher temperatures were employed. Moderate quantities of this steel are still made. The compositions vary considerably, as is evident from the following analyses, but all of them contain high percentages of carbon and manganese:

C.	Si.	Mn.	Cr.	W.	Mo.
1·80	0·56	1·80	1·60	7·30	4·58
2·25	0·50	1·50	2·00	12·00	—

Self-hard steel was the forerunner of modern high-speed steel. The latter is to a great extent self-hardening, but it was found that by decreasing the carbon and manganese and increas-

ing the tungsten, a hardening operation then resulted in the production of a material possessing extraordinary cutting properties at very high speeds.

In order to treat a high-speed steel effectively, a hardening temperature between 1250° and 1350° C. must be employed. After quenching, whether in water, oil, or air, the hardness may be still further increased by reheating to about 550°–650° C., this treatment giving rise to what is known as " secondary hardness ".

Chromium in high-speed steel increases the secondary hardness and also lowers the hardening temperature. Too high a chromium content, however, causes difficulty in forging and rolling, and most modern steels contain between 3 and 4·5 per cent.

Manganese is generally present in small amounts only, in view of the tendency for the element to cause cracking when the steels are quenched in oil or water. This element also increases the air-hardening tendency, hence the steel in the forged condition may be decidedly hard and require careful and prolonged annealing to facilitate any subsequent machining. The manganese content rarely exceeds 0·3 per cent, and steels containing traces only are quite common, but in the author's opinion a manganese content of 0·15 to 0·25 per cent should always be aimed at.

Silicon apparently has no harmful effect up to about 0·4 per cent, but greater quantities may give trouble. Any abnormal silicon content is generally due to that of the alloys used in the manufacture of the steel.

Tungsten may be regarded as the dominating constituent of high-speed steel, both with regard to quality and price; and in general, the steels fall into one of two classes containing 14 and 18 per cent tungsten respectively. The carbon content is much less than in self-hard steel, with the consequence that less difficulty is experienced in working. For the same carbon content, the 18 per cent tungsten steels are harder than the 14 per cent type, and to balance matters somewhat the carbon content for the latter, in general, varies between 0·65 and 0·8 per cent as against 0·55–0·7 per cent for the 18 per cent types. In regard to the carbon content, however, some consideration of the method of hardening is necessary. 14 per cent tungsten steels containing more than 0·7 per cent carbon tend to crack when quenched in water, whereas oil-quenching is quite safe, and water-hardening steels seldom contain more than 0·65 per cent carbon.

Vanadium is added to these steels up to 1·5 per cent, and as

little as 0·5 per cent vastly improves the cutting qualities of the tools. Above 2 per cent vanadium, the steels become very hard and brittle, and no improvement in properties is obtained which is worth the increased cost. Vanadium high-speed steels air-harden to a much greater extent than those free from the element.

Molybdenum high-speed steels seldom contain more than 2·5 per cent Mo, and, as originally pointed out by J. O. Arnold, these steels are rather erratic in their behaviour as tools in the absence of vanadium. The latter appears to act as a stabilizer, and molybdenum high-speed steels generally contain at least 1 per cent vanadium also. Such steels seldom require any other method of hardening than cooling in air from a high temperature.

Cobalt is often added to " super high-speed " steel in quantities up to 12 per cent. These steels are hardened in air, but a satisfactory hardness can only be obtained with a sufficiently high carbon content, and steels containing 0·8–0·85 per cent carbon are quite common. There is apparently a critical carbon content for these super high-speed steels containing large proportions of the alloying elements, below which it is impossible to harden the steel so as to render it suitable for tools, and many cases of failure have arisen which could only be attributed to a deficiency of carbon. This deficiency is sometimes indicated by a flaky appearance in the fracture of the cogged or rolled bars.

Sulphur and phosphorus do not exert so harmful an effect on the properties of these steels as on those of plain carbon steels; but neither element should exceed 0·06 per cent, since major segregation may result from these elements being present in much larger quantities in the centre of the ingot. This segregation then persists throughout forging and rolling, and although it may cause no trouble in such articles as milling cutters, the segregated centre becomes the actual cutting portion in the case of a twist drill, and if segregation is very pronounced failure of the drill is almost inevitable. In addition, the articles may crack during hardening. The difficulty in keeping the two elements down to the desired values is due to the fact that the alloys used in the manufacture of the steel frequently contain appreciable amounts of them. High-speed steel melts very slowly, with the consequence that in the ordinary crucible process a fair quantity of sulphur is absorbed from the sulphurous gases from the coke. To a certain extent the sulphur content serves to indicate the source of the chief materials used in manufacture. This sulphur difficulty does

not arise if the steel is made in the high-frequency electric furnace

In the melting of high-speed steel in crucibles there is the possibility that liquation may occur, i.e. the liquid metal may separate into layers. The lower layers, in virtue of their greater density, are then richer in tungsten than the upper layers, and when cast the resulting ingot may show considerable differences in composition from one end to the other. The effect may be accompanied by very pronounced carbide segregation, which persists throughout forging and rolling, and then causes the material to split when hardened. This certainly represents bad melting practice, but should always be looked for in cases of failure of batches of high-speed tools.

Typical compositions of some modern high-speed steels are given in the following table:

C.	Si.	Mn.	S.	P.	Cr.	W.	Mo.	V.	Co.	Type.
0·68	·20	·27	·032	·030	3·26	14·51	—	—	—	Water or oil-hardening.
0·66	·25	·13	·057	·005	4·30	14·20	—	·56	—	,, ,, ,,
0·69	·20	·10	—	—	3·60	18·00	—	·71	—	Oil or air-hardening.
0·65	·20	tr.	·030	·020	4·50	18·00	2·01	1·03	—	,, ,, ,,
0·70	·35	·08	·020	·017	4·30	16·18	0·92	·87	4·00	Air-hardening.

Treatment of High-speed Steel.

The structure of a high-speed steel is, in reality, very complex. Stable double carbides are formed, whilst most of the tungsten exists in combination with iron as tungstide of iron Fe_3W_2. The double carbides, however, are mutually soluble even in the solid state, and the resulting solid solution or " complex " carbide exhibits a simple microstructure, and hence may be regarded as a single constituent. Further, the tungstide of iron, together with other elements not combined with carbon, enters into solid solution with iron, with the consequence that the metallography of high-speed steel is relatively simple. Thus Grossmann [*] and Bain have shown that these steels may be considered as members of a simple binary system (fig. 118), and the very slow rate at which diffusion occurs during solidification results in production of a very pronounced cored or dendritic structure in the cast condition (fig. 119 (a)). Further, this heavy coring gives rise to the existence of some eutectic, although the steel may be represented by a composition to the left of A. The structure, as would be expected from the above diagram, shows some resemblance to

(a)
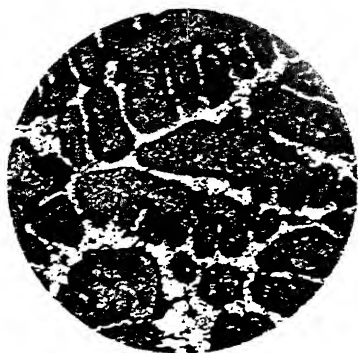
(b)
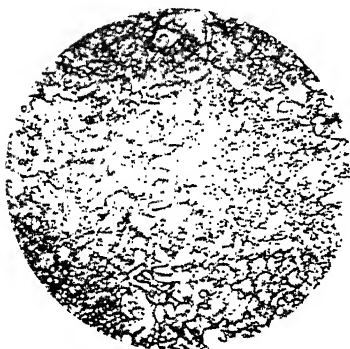
(c)

(d)

Fig. 119.—High-speed steel (18 per cent tungsten) in different
stages of treatment

(a) As cast. ×250. The lighter areas are the eutectic.

(b) The same specimen after being annealed. ×250. Note
    that the eutectic has decreased in quantity and has
    lost some of its continuity.

(c) After forging. ×500.

(d) Finished, rolled, and annealed. ×500.

that of a white cast iron. The eutectic is very hard, but extremely brittle, and the steel is therefore brittle when in the cast state. The eutectic must be broken up and the cored structure destroyed before the steel is hardened, otherwise it will crack. The necessary structure can be obtained only by careful mechanical and thermal treatments.

After casting, the ingot is slowly heated to about 800°–850° C., and thoroughly annealed by maintaining at this temperature for 24 hours. The steel is then allowed to cool down in the furnace over a period of about 18–24 hours. This treatment considerably modifies the cored structure, and in addition, diminishes the quantity and tends to destroy the continuity of the eutectic. The liability to cracking during forging is thereby lessened. For forging, the steel is again slowly heated to a dull red heat, and then more rapidly to an orange-red (about 1100° C.). Forging should not be con-

Fig. 118.—Simplified Constitutional Diagram for High-speed Steels

tinued below a bright red heat (about 900° C.), and the steel must be reheated as often as is necessary to maintain the temperature above this value. High-speed steel must be thoroughly worked if the most satisfactory results are to be obtained. Insufficient work, particularly if the material is finished by rolling, may lead to the formation of " strings " or laminations of carbide; and when these are present in such articles as milling cutters the teeth break off in use. In addition, carbide laminations tend to induce cracking during heat-treatment. The effects of the above treatments on the microstructures are illustrated in fig. 119 (a), (b), (c), (d). After forging, the articles should be placed, whilst still hot, in a furnace at 800°–850° C., and when thoroughly soaked they are cooled in the furnace, i.e. at a relatively slow rate.

High-speed steel should be cut off when it is hot, or sawn

cold. If the steel is broken when cold, the material tends to split and develop longitudinal cracks.

The Brinell hardness in the annealed state is about 250–300, and the steel is then easily machined.

The Hardening of High-speed Steel.

Cold high-speed steel should never be placed in a hot furnace, otherwise it tends to crack, and tools are therefore warmed on the top of the furnace or a hot plate. They are then transferred to a furnace at about 800°–850° C., and after they are thoroughly soaked are placed in the actual hardening furnace, which is maintained at a temperature of 1150°–1300° C. The hardening temperature depends on the size, shape, and composition of the steel. The higher carbon steels are heated to the lower temperatures, whilst higher temperatures must be employed for the more massive parts. The steel must be brought to the hardening temperature as rapidly as possible, and quenched immediately the tool has reached this temperature. If the steel is of the air-hardening type, it is important that the air-blast employed should be free from moisture, otherwise the steel will tend to crack.

For hardening, different types of furnaces are employed. If the furnace uses gas and compressed air the flame should not be allowed to come into contact with the steel, and a pyrometer should always be used where possible. Very satisfactory results are obtained by the use of an electrically heated bath of molten barium chloride, in which the articles are immersed. Water is rather too drastic a quenching medium for many high-speed steels, and its use is generally restricted to the hardening of the 14 per cent W steels in cases where only the actual cutting edge requires hardening. Oil is a much less drastic quenching medium, but some of the " super " high-speed steels tend to crack when oil-quenched. Molten lead forms a very effective quenching medium in such cases, the final cooling being carried out by burying the tools in dry sand. With some of these steels, quenching in molten lead or in a dry air-blast is imperative.

The microstructure of a hardened high speed steel consists of isolated spherical particles of the complex carbide embedded in an austenite matrix. Austenite, however, is relatively soft, and if no further treatment is given, the tool does not behave at all well when first brought into service, and the cutting edge has a very short life. When it is reground and once more placed in the

machine, satisfactory results are obtained however. This is due
to the fact that after the cutting edge has failed considerable heat
is developed by the rubbing of the tool against the material which
is being machined, and some of the austenite in the surface layers
is transformed into hard martensite. After the second grinding,
therefore, the actual cutting edge consists of hard carbide particles
in a martensite matrix. At one time this initial failure of a high-
speed tool was regarded as inevitable, but nowadays it is usual
to bring about the austenite-martensite transformation by what is
really a *tempering* treatment. As distinct from carbon steels,

tempering increases
the hardness of high-
speed steel, as will be
evident from fig. 120.
The effect is known
as " secondary hard-
ness ", and although
the temperature cor-
responding with maxi-
mum hardness varies
with different steels,
they are generally
tempered at about
550°–600° C. before
being put into use as
tools. If higher tem-

Fig. 120.—Hardness Curve of 18 per cent Tungsten
" Super " High-speed Steel after being hardened and
then reheated to various temperatures.

peratures are employed, the hardness rapidly falls, as will be
observed from the curve. It should be noted that although
hardness tests do not indicate the cutting properties of a tool, as
will be evident from the fact that some hardened plain carbon
steels give higher values than many high-speed steels, such tests
certainly serve to indicate whether a given steel has been effectively
heat-treated.

The sharp rise in the above hardness curve is due to the partial
re-solution of some of the carbide which has been deposited
during " tempering ".

Typical microstructures are shown in fig. 121 (*a*) and (*b*),
whilst fig. 122 shows the structure of a " burnt " steel in which
the eutectic has been re-formed. This is generally due to an ex-
cessively high hardening temperature, but may also be caused by
holding the material at a correct temperature for much too long a

time. The steel is then excessively brittle. Such structures are generally the result of haphazard treatment such as when the hardening is carried out in a smith's hearth. On this account, also, the heating of a tool until the nose begins to " sizzle ", which is so often advised, cannot be too strongly deprecated.

High-speed steel is a remarkable material, but the greatest care must be taken in its treatment if the best results are to be obtained.

Other Tungsten Alloys used for Tools.

Within the last few years several new alloys, sold under trade names such as " Widia ", " Carballoy ", &c., have been introduced for tips of turning tools. Tungsten carbide is the basis of these alloys, although this substance is too brittle by itself, and is usually associated with varying amounts (up to 15 per cent) of chromium and cobalt. These elements yield a material having a fine porcelain fracture which does not splinter as does the tungsten carbide itself. The alloys possess a greater cutting power than high-speed steel, and are now being employed for the machining of chilled rolls and " Hadfield's " manganese steel, and may even be employed for putting threads on glass vessels. The material must, however, be treated with the greatest care and " chattering " of the tool entirely avoided, otherwise the cutting edge readily breaks off. For this reason, much more massive and rigid tool-holders are necessary. These alloys are very expensive, and ordinary carbon steel tools are therefore tipped with the material. The Vickers hardness of " Widia " is above 1100.

Case-hardening Steels.

For many engineering purposes, certain machine parts are required which must have an extremely hard surface to resist wear and a very tough interior or " core " to resist shock. Case-hardened parts are therefore made from low carbon steels, and, after being machined to the desired shape, are packed in some material rich in carbon and then heated to a temperature above 900° C. Carbon then diffuses into the outside layers, and the ultimate product is a material consisting mainly of a steel of the original composition enveloped by a " case " containing about 0·9 per cent of carbon (fig. 123). By varying the temperature and the duration of heating, almost any desired thickness of case may
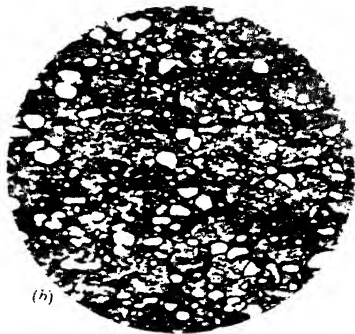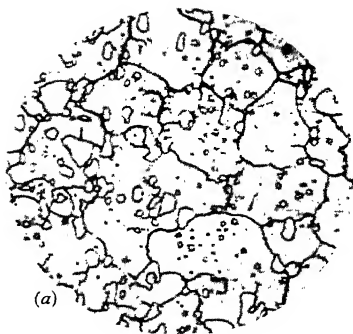
Fig. 121.—Microstructures of "super" high-speed steel containing 18 per cent tungsten and 5 per cent cobalt. · 1000

(a) Oil-quenched from 1325° C. Complex carbide embedded in austenite matrix. Vickers hardness 870.
(b) Oil-quenched 1325° C.; reheated to 600° C. for 10 minutes. Shows breakdown of the austenite. Vickers hardness 870.

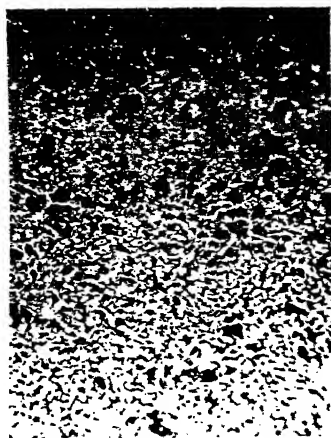Fig. 122.—"Burnt" high-speed steel which cracked in hardening. × 500

Fig. 123.—Case-carburized steel showing gradual change in carbon content from the outside to the interior. × 40.

be obtained, but generally a depth of from 1 to 2 mm. is aimed at. After carburizing, the materials are heat-treated in order to obtain the best combination of hardness in the case and toughness in the core.

Owing to their low carbon contents, case-hardening steels are very readily machined, and this, to a great extent, accounts for the popularity of such steels amongst engineers. Easy machining does not necessarily imply good machining properties, and in this connexion the structure of the steel is of the greatest importance. If the pearlite in it exists in comparatively large isolated masses, the steel tends to tear during machining, and a poor finish is obtained. The surface then contains what are really machining cracks which develop still further when the steel is hardened. For this reason, a plain carbon case-hardening steel should not be annealed for machining. In many cases, the " as rolled " bars present little difficulty, but forgings and stampings should always be normalized in order to obtain small uniformly distributed pearlite areas.

Plain carbon steels may be divided into three main classes:

(a) 0·08–0·14 per cent carbon—used for purposes where an extremely tough core is desired, and for articles of thin section.

(b) 0·13–0·2 per cent carbon—ordinary case-hardening steel and the type generally employed.

(c) 0·22–0·3 per cent carbon—used where greater strength of core is desired, such as in ball and roller bearings.

In addition to carbon, the manganese content of the steel is very important, and in view of the great difficulty in deoxidizing such low carbon steels, a fairly high manganese content is essential as an insurance against ferrous oxide. Manganese also aids in the carburization, and in the very low carbon steels should not be present in less quantity than 0·75–0·8 per cent. At the same time, however, it must be remembered that manganese intensifies the quenching effect on the case when the steel is subsequently hardened, and in the higher carbon steels this may lead to the development of hardening cracks in the case. Steels containing more than 0·2 per cent carbon should not contain manganese in excess of 0·6 per cent. In electric steels, where the deoxidation is more complete than in open-hearth steels, a higher manganese than 0·55 per cent is unnecessary.

Silicon tends to retard casing, but improves the impact values

of the heat-treated specimens. The element is generally kept below 0·35 per cent, however, in plain carbon steels, in view of its tendency to induce graphitization during the carburizing period.

Carburizing.

It has been mentioned that the length of time that the steel is in contact with the carburizing medium has a marked effect on the depth of case obtained, as also the temperature maintained throughout the operation. The carburizing medium itself is, however, of primary importance, as will be evident from the following data, due to G. Shaw-Scott: *

Time of Heating at 900° C.	Charred Leather.	Wood Charcoal.	Wood Charcoal and Barium Carbonate.
2 hr.	1·15 mm.	0·72 mm.	1·36 mm.
4 ,,	1·58 ,,	1·07 ,,	2·20 ,,
8 ,,	2·30 ,,	1·58 ,,	2·80 ,,
12 ,,	2·80 ,,	1·80 ,,	3·17 ,,

At one time, various cyanogen derivatives such as potassium ferrocyanide—" yellow prussiate of potash "—were commonly employed as constituents of case-hardening compounds. Their use has, however, been almost entirely dispensed with, since in many instances the gases evolved on heating developed such pressures that the lids and seals of the boxes in which carburization was carried out became displaced, and allowed access of air. There is little doubt that charred leather owes its efficacy to its nitrogenous as well as its carbonaceous nature, whereas barium carbonate decomposes and ensures an atmosphere of carbonaceous gases in contact with the steel, which promotes ready carburization.

Mixtures are commonly employed, and their compositions vary considerably, but when once a particular mixture has proved satisfactory it is advisable to adhere to it if uniform results are to be expected. A mixture giving excellent results consists of about 35–40 per cent barium carbonate with wood charcoal. A mixture once used should never again be employed alone, although a certain proportion of it may be mixed with new material without much detriment.

In some circumstances, particularly when it is desired to case-harden certain parts only, " cyanide hardening " may be employed. This is effected by immersing the articles in some molten cyanogen compound—generally potassium cyanide—for about

15 minutes, and, on withdrawal, quenching the articles in water. Temperatures between 870° and 900° C. are usually employed, and the method is advantageous because it is quick and reduces treatment costs. The greatest disadvantage associated with cyanide hardening is due to the extremely poisonous nature of the materials used and gases evolved.

Sometimes, also, the articles are smeared with a paste of some such material as the above, heated to about 900° C., and then quenched. This, however, only exerts a superficial case-hardening effect, and cannot be recommended in those instances where a considerable depth of case is desired.

Usually the articles to be case-hardened are packed in boxes, and it is important that they should be separated from each other and from the sides and lid by at least 2 in. of the carburizing medium. The box lid should be luted with clay or, what is perhaps better still, " wheelswarf " from the grindstone. The boxes were at one time made of cast iron. With repeated heatings, however, cast-iron boxes scale and distort to such an extent that the lids cannot be fixed so as to obtain perfectly air-tight coverings, and it is always advisable to employ boxes made from Ni-Cr-Fe alloys containing from 10 to 20 per cent of chromium and from 30 to 60 per cent nickel. Although the initial cost is considerably greater, this is more than counterbalanced by their longer life and lack of distortion, whereby perfectly air-tight coverings are assured even after repeated heatings.

Before being placed in the boxes, the articles should be thoroughly cleaned in order to allow of even penetration of the carbon, and thus ensure a more uniform thickness of case. Surfaces which are not required hard, such as the threads of screwed parts, are protected by coating them with some material which does not absorb carbon. The results obtained with ordinary clay are not very satisfactory, but a thick paste made from pulverized asbestos which has been ignited, fire-clay, and water gives better results. The paste must of course be allowed to set, and be perfectly free from moisture before the articles are packed in the box. Copper-plating is often employed for the same purpose, a thickness of about 0·003–0·004 in. being quite effective in preventing any carburization of the steel underneath. Much thicker deposits are not advisable, since the copper may flake off during heating.

It has already been mentioned that γ iron is the only form capable of dissolving carbon to any appreciable extent, and the

temperature employed in casing must therefore be sufficiently high to ensure that the steel consists entirely of austenite (fig. 124). The standard temperatures for casing are between 900° C. and 930° C. At such temperatures diffusion of the carbon readily occurs, and for most purposes, a soaking period of about five hours will yield a case of sufficient depth. After casing, the articles are cooled down in the furnace.

Heat-treatment of Case-hardened Parts.

After the articles have been removed from the boxes, they should be thoroughly cleaned before being heat-treated. The
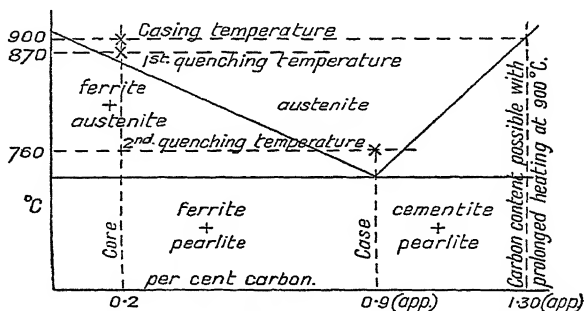
Fig. 124.—Constitutional Diagram for Commercial Steels, showing temperatures employed in case-hardening

material may now be regarded as being composed of two distinct steels—the " case ", containing about 0·9 per cent carbon, and the " core ", containing, say, 0·2 per cent—and in order to obtain the most satisfactory results, two separate quenching treatments are necessary.

First Quenching.

As a result of prolonged heating at a high temperature during the carburizing operation, grain growth occurs in the core to a very marked extent, and the core therefore shows the typical gross angular structure of an overheated steel (fig. 125 (a)). This structure is destroyed, and the core " refined ", by heating to such a temperature that the whole of the free ferrite is taken into solution. This necessitates a temperature above the upper critical point for the core (fig. 124), and the material is heated to 860°–

870° C., thoroughly soaked at this temperature, and then quenched in water. The structure then consists almost entirely of martensite (fig. 125 (*b*)), although the core may show minute particles of ferrite which have been precipitated during quenching and which may be surrounded by troostite. Both the case and the core are much too brittle after this treatment. The case is coarsely martensitic owing to the fact that the temperature at which the material has been quenched is much too high for a steel of its composition, whilst the preponderance of martensite in the core is altogether undesirable on account of its low resistance to shock. The articles are therefore submitted to a second treatment.

Second Quenching.

The temperature of quenching in this instance is that which is normally employed for a tool steel containing about 0·9 per cent carbon. The earlier stages of this second reheating may be regarded in the nature of a tempering treatment, during which the martensite is converted into sorbite where the carbide particles are very small and evenly distributed. Some coalescence of the carbide takes place as the temperature is raised, but if the heating period is not unduly prolonged, a very fine structure persists throughout. At the critical point, therefore, small crystals of austenite are re-formed, and the temperature of quenching generally employed (about 760° C.) is such that no appreciable amount of grain growth occurs; and, on quenching a second time, the case consists of a very fine martensite which is hard but not excessively brittle.

During this second treatment, analogous changes are induced in the core, but since the carbon content is low, the structure consists (at 760° C.) of very small austenite crystals embedded in a matrix of the excess ferrite, and, after quenching, the material consists of small areas of martensite with small ferrite crystals surrounded by troostite (fig. 125 (*c*)). The core should not be soaked at this second quenching temperature, and it is an advantage to reheat the material as quickly as possible, particularly throughout the range 700°–760° C. Excellent results are obtained by heating rather slowly in a furnace at a temperature of about 600° C., and then transferring the articles to another furnace already at 760° C., and as soon as the case attains this temperature the steel is quenched. By this means a temperature gradient exists in the specimen at the moment of quenching, and the amount of

martensite in the core is then reduced to an absolute minimum, with the consequence that the core is in the toughest possible condition. Tempering at about 150° C. is advisable, particularly with articles of thin section. This relieves hardening strains in the case without any appreciable effect on the hardness.

Alternative Treatments of Case-hardened Parts.

The double treatment outlined above is the only one which can be recommended to yield entirely satisfactory results for most purposes. In order to reduce treatment costs, however, simpler treatments consisting of one quenching only are often employed.

Quenching from the casing temperature without allowing the materials to cool down slowly should only be used for very ordinary purposes where hardness is the chief requirement. The coarse martensitic character of both case and core after such treatment results in a tendency to failure due to brittleness.

One quenching from a temperature between the upper and lower critical points for the core is commonly employed. After cooling from the casing temperature, the steel is reheated to 800°–830° C. and quenched in water. The whole of the excess ferrite is therefore never taken into solution during heating, but much of it remains as a skeleton of the original overheated structure produced during the carburizing operation. The final structure of the core thus consists of comparatively large isolated masses of ferrite " ringed " with troostite in a martensite matrix (fig. 126). The case is certainly hard, but the core is not so tough as is desirable, and thin sections are readily fractured.

The appearance of the fracture of a case-hardened steel is one of the best indications as to whether suitable treatment has been given to it. When properly treated, there is apparently a sharp line of division between case and core, and whereas the latter shows a distinctly fibrous fracture, that of the case is smooth and fine-grained and typical of a correctly hardened tool steel. The depth of casing is readily observed, and its hardness determined by means of a smooth file. A plain carbon steel should be so hard that the case cannot be scratched with the point of a new file.

The influence of the final treatment on the appearance of the fracture is illustrated in fig. 127. The coarseness of the " grain " in both the case and the core of the specimen subjected to the single quenching treatment is clearly shown, particularly if the

(a)

Fig. 126.—Core of case-hardened steel (C, 0·2; Mn, 0·8) "cased" at 900° C., reheated to 820° C., and quenched in water. × 250.

(b)

(c)

Fig. 125.—Core of case-hardened steel (C, 0·2 per cent; Mn, 0·8 per cent).
(a) After "casing" at 900° C., followed by slow cooling.
(b) Quenched from 870° C. in water.
(c) Quenched 870° C.; reheated to 760° C. and again quenched in water.
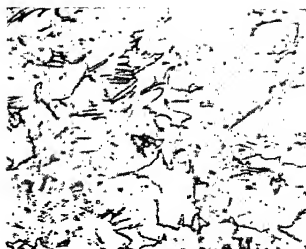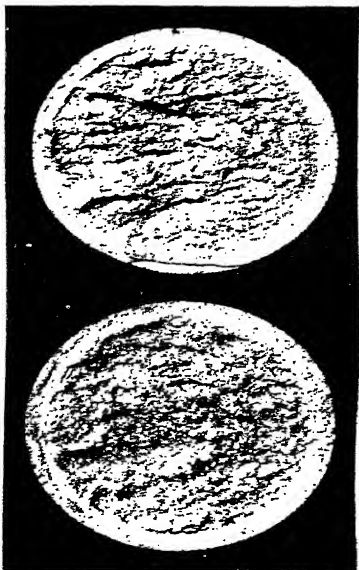All magnified 250 times.

(b)

Fig. 127.—Fractures of case-hardened bars after being subjected to the following treatments:

(a) W.Q. 875° C.; W.Q. 760° C. Hardness (Vickers diamond): Case 803, Core 221.
(b) W.Q. 825° C. Hardness (Vickers diamond): Case 870, Core 221.

photographs are examined with the aid of a small hand lens. Several blows with a heavy sledge-hammer were necessary to fracture the piece which had been doubly quenched, whereas a single blow sufficed in the case of the other specimen.

When slowly bent, the case cracks, but the core tends to resist fracture, and with a well-treated steel a bending angle of several degrees is often obtained before complete fracture occurs (fig. 128).

The tempering of case-hardened parts is to be recommended for most purposes. The temperatures employed are generally between 150° and 200° C., and whilst such treatment has very little effect on the hardness of the case, hardening strains are released, and both case and core toughened somewhat.

Causes of Failure in Case-hardened Parts.

The failure of a case-hardened steel may be due to causes other than those, such as slag inclusions, rokes, unsuitable composition, &c., which are common to all steels. This arises from the fact that a composite steel is being dealt with, and that its treatment is, in reality, a very complex one. Soft spots on the surface may be due to several causes:

(*a*) The presence of dirt and grease on the surface during any stage of the treatment. This may result in uneven penetration of the carbon during casing, or in a decreased intensity of hardening during quenching.

(*b*) Insufficient time allowed during casing, particularly when allied with careless packing in the carburizing medium, may yield a thin case of very varying thickness. In parts the case may then be so thin that it is completely removed during the final grinding.

(*c*) Soaking too long at either quenching temperature may result in decarburization of the skin to such an extent that it is not removed in grinding.

" Flaking " or " peeling " is a frequent source of trouble. The outside skin or case cracks and then peels off as shown in fig. 129. If the diagram on p. 162 is again examined, it will be obvious that at the temperatures normally employed in casing, γ iron is capable of dissolving much more than 0·9 per cent of carbon. Under ordinary circumstances, however, diffusion of carbon into the interior takes place at such a rate that the production of a case containing more than this amount of carbon is avoided. With prolonged heating and the formation of a deep case, the extreme surface

layers take up carbon at a greater rate than that at which diffusion occurs into the interior, with the consequence that after cooling the structure is observed to consist of a network of free cementite enclosing the areas of pearlite. The same effect is produced by casing at too high a temperature, although the case may not be abnormally thick. If such a material is subjected to the " double " treatment, the free cementite may be taken into solution, but the case is then excessively brittle, whilst if one quenching only is employed, the cementite persists in the form of a network around the areas of martensite (fig. 130), and again, in consequence, the steel is very brittle. This carbide network may also lead to the development of surface cracks when the articles are being ground to finished size (fig. 131).

Too great a depth of case may result in failure, even in the absence of free cementite, particularly if the articles are of thin section, such as, for instance, with case-hardened gears. The thickness of the case is then at the expense of the core, and in extreme circumstances the material may be almost coreless.

The final grinding of case-hardening parts is an operation requiring considerable care. The use of a wheel of too coarse a texture, or an inadequate supply of water during grinding, may lead to the development of minute surface cracks, or the formation of soft spots as a result of the tempering effects due to localized generation of heat.

Alloy Case-hardening Steels.

The principal alloying element introduced into case-hardening steels is nickel, with which, however, chromium is very often associated, and in some instances a small proportion of vanadium (up to 0·2 per cent) is also present. Experience has proved that no great benefit is derived if the nickel content is much less than 3 per cent, but steels containing 3–3·5 per cent nickel, either with or without chromium, are employed for a great variety of purposes. In special circumstances, particularly where extreme toughness in both case and core is desired, a steel containing about 5 per cent of nickel may be employed with very beneficial results, whilst steels containing 6–7 per cent of the element are sometimes used for very special purposes.

Nickel influences the properties of case-hardening steels in several ways. In the first place, for steels of the same carbon content, the temperatures at which nickel steels become entirely

Fig. 128.—Showing cracks induced in case of a well-treated case-hardened steel when slowly bent. Treatment: W.Q. 875° C.; W.Q. 760° C.; Td. 150° C.

Fig. 129.—Showing " exfoliation " or peeling in a case-hardened part—a frequent source of trouble

Fig. 130.—Cementite network in " case " of case-hardened roller-bearing which failed after only 38½ hours at 320 revs. per min. × 200.
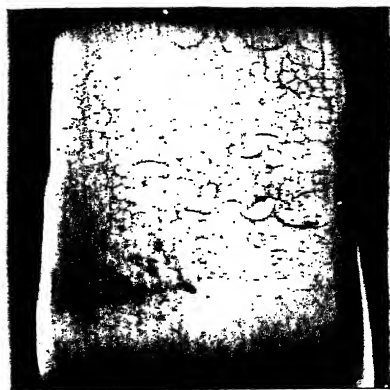

Fig. 131.—Showing grinding cracks on surface of case-hardened cam

austenitic are lower than those for the nickel-free steels. This is evident from the diagram given on p. 126. For this reason, it might be expected that a nickel steel would carburize more readily at a given temperature than a plain carbon steel of about the same carbon content. Nickel, however, hinders diffusion of the carbon, and to such an extent that the actual time necessary for a given depth of case is longer than that required for a nickel-free steel, although a higher casing temperature can be employed with less harmful effects. When correctly treated, the carbon content of the case of a nickel steel is considerably below 0·9 per cent, and after being heat-treated the hardness of the case, as measured by the usual indentation tests, is not nearly so great as that of a plain carbon steel. Nickel case-hardened steels, however, are characterized by their remarkable resistance to wear, particularly when subjected to any rolling action. Nickel also lowers the critical hardening speed to such an extent that a sufficiently hard case can often be obtained by quenching in oil instead of water, with a consequent reduction in the amount of distortion.

One of the greatest advantages associated with the use of nickel in case-hardening steels is due to its restraining influence on grain growth during the carburizing treatment, with the consequence that the structure of the core of a case-carburized nickel steel is not nearly so coarse as that of a corresponding plain carbon steel; and for many purposes the usual preliminary quenching treatment for the refinement of the core may be dispensed with. This will be evident from the following tests on a steel containing 0·14 per cent carbon and 3·33 per cent nickel, after being heated for four hours at 910° C., cooled in air, and then subjected to the treatments specified: *

Treatment.	Y.P., tons per sq. in.	M.S., tons per sq. in.	Elongation on 2".	Reduction of Area, per cent.	Impact, ft.-lb.	Brinell No.
O.Q. 850° C. O.Q. 760° C.	24·4	36·6	37·0	67·8	94, 90, 90	153
O.Q. 760° C.	23·9	35·5	35·0	63·7	90, 90, 88	153

It will be observed that the difference in properties is almost negligible, although it is rather more pronounced when the steels are quenched in water. If the most satisfactory results are to be obtained, a double quenching treatment should always be adopted. With any treatment, however, much greater uniformity can be obtained with a nickel steel than with a plain carbon steel.

* " Case-hardening and the use of Nickel Steels ", *Mond Nickel Bulletin*, B.1.

As already indicated in the section on nickel steels, nickel increases the tensile strength of ferrite without, however, seriously affecting the ductility. Consequently, the core of a case-carburized nickel steel is stronger and more tough, after heat-treatment, than that of a nickel-free steel. The best results for most purposes are only obtained, however, with a carbon content not greater than 0·15 per cent since otherwise the impact values for the core may be much lower than is desirable. Generally, if used for similar purposes, the carbon content in a nickel steel is lower than that of the plain carbon steel.

The manganese content of a nickel case-hardening steel is also of great importance. It must be remembered that it is exceedingly difficult to bring about the thorough deoxidation of any very low carbon steel, and in this respect nickel steels apparently give much more trouble than nickel-free steels. Consequently, a fairly high manganese content is essential as an insurance against ferrous oxide, and the quantity of the element should not be below 0·5 per cent. Up to 0·7 per cent manganese may be employed with markedly beneficial results, since, in addition to its deoxidizing properties, it assists in the carburizing operation, and thus tends to counteract the obstructing influence of the nickel on the diffusion of the carbon. The carbon gradient from core to case is then much less pronounced in such steels than is sometimes observed in nickel steels of lower manganese content, in which " peeling ", due to the fact that there exists too sharp a line of demarcation between case and core, is a frequent source of trouble.

Nickel-chrome Case-hardening Steels.

These steels may be divided into several classes such as are indicated in the following table, in which average mechanical test results for typical plain carbon and plain nickel steels are also given. These values were obtained on the uncarburized bars, which, however, had been subjected to the usual double water-quenching treatment for case-hardened steels.

	C.	Mn.	Cr.	Ni.	M.S., tons.	Elonga-tion.	Reduction of Area.	Impact, ft.-lb.
(a)	0·10–0·15	0·35–0·50	0·25–0·60	3·0–3·50	55–70	14–18	30–40	35–45
(b)	0·08–0·15	0·35–0·45	1·00–1·50	3·0–3·50	70–90	10–15	35–45	25–35
(c)	0·08–0·12	0·35–0·45	0·25–0·50	4·0–4·50	75–85	10–15	35–50	20–30
(d)	0·08–0·12	0·30–0·40	1·00–1·50	4·0–4·50	75–95	10–15	35–50	20–35
	0·08–0·20	0·70–0·85	—	—	25–45	25–40	50–70	50–100
	0·10–0·15	0·40–0·50	—	3·0–3·25	45–55	25–30	40–60	55–80
	0·08–0·15	0·40–0·45	—	4·50–5·0	70–80	15–20	35–30	20–30

A lower manganese content is required in a nickel-chrome case-hardening steel than in a plain nickel steel. This is partly due to the fact that chromium serves a similar purpose to manganese in assisting casing and in counteracting the tendency for nickel to induce graphitization of the carbon. Higher manganese contents than those specified in the foregoing table may give rise to the development of cracks in the case during heat-treatment.

Chromium exerts a very pronounced effect on the properties of the core of a case-carburized nickel steel, the tensile strength being improved without seriously lowering the ductility and impact values. The most beneficial effect due to the introduction of chromium is, however, the very marked improvement in the wear-resisting properties of the case.

Chrome-nickel case-hardening steels are not nearly so susceptible to the mass effect on heat-treatment as either the plain carbon or the plain nickel steels. This will be evident from an examination of the following test results on the heat-treated specimens:

Composition of Steel.	Size of Piece Treated.	Y.P., tons per sq. in.	M.S., tons per sq. in.	Elonga- tion, per cent.	Reduction of Area, per cent.	Impact, ft.-lb
C, 0·16; Mn, 0·80	0·564″ dia.	38	47	14	46	41
	1·000″	35	45	27	59	90
	2·000″	29	33	30	61	84
C, 0·15; Mn, 0·43 { Cr, 0·51; Ni, 3·02 {	0·564″	69	78	12	47	45
	1·000″	55	66	16	48	64
	2·000″	50	58	21	52	56

Steels of composition (a) in the table of compositions on p. 168 are suitable for all general case-hardened purposes, whilst those of class (b) may be used for highly stressed parts such as those for roller bearings, gudgeon pins, &c. Class (c) steels are useful where a very high tensile strength, combined with great toughness, is essential. The high-nickel high-chrome steels of class (d) are generally recommended for parts of intricate and varying section, in view of the fact that very uniform structures are obtained; and since oil-quenching is sufficiently drastic for most purposes, distortion as a result of heat-treatment is reduced to a minimum. The carbon content of such steels is of the greatest importance, and the lower the carbon the better are the results obtained. With 5 per cent nickel and 0·25 per cent carbon, the core consists entirely of martensite even when subjected to the " double " treatment, and is then much too brittle for most purposes. Experience has shown that 0·15 per cent of carbon should be regarded as a maximum for this type.

The temperatures employed in the carburization of nickel and nickel-chrome steels are generally between 900° and 940° C., the higher temperature being employed when a considerable depth of case is desired. In view of its excellent wearing properties, however, a thinner case often suffices in a nickel-chrome steel than if a plain carbon steel were used for the same purpose.

When subjected to the " double " treatment, temperatures between 830° and 850° C. are employed for the first quenching, the higher temperatures being used for the lower-chromium 3 per cent nickel steels. This treatment is then followed by a reheating to and a quenching from about 750°–760° C.

If a single quenching treatment is desired, quenching from about 800° C. yields a fairly tough core together with a good hard-wearing case. Nickel-chrome case-hardened steels are often tempered at about 150°–200° C. This treatment relieves quenching stresses, but has little effect on the hardness of the case. Higher tempering temperatures should not be employed, otherwise " temper-brittleness " may be induced in the core.

The Effect of Nitrogen on Steel, and the Case-hardening of Steel by Nitrogen.

The hardening effect of nitrogen on iron and steel, and its consequent embrittling influence, have been known for quite a long time, and several cases of failure have been traced to the presence of abnormal quantities of this element in the materials.

Normally, the quantity of nitrogen in steel is very small, and does not adversely affect its properties. High-temperature welding, such as when the electric arc is employed, may increase the nitrogen content to such an extent that the material is exceedingly brittle in the vicinity of the weld. Again, the inferior properties of Bessemer steels as compared with Siemens steels are in all probability entirely due to the difference in nitrogen content. " Armco " iron forges well at high temperatures and is very tough at low temperatures, but between 800° and 900° C. is very brittle, a fact which has also been attributed to the presence of nitrogen; and the belated failure of some boiler plates has been put down to this same cause.

It is only comparatively recently that the hardening effect of nitrogen on steel has been fully exploited in case-hardening. Nitrogen alone has very little effect on steel, but if the steel is heated in an atmosphere of ammonia vapour, the nitrogen of the

ammonia readily combines with the iron to form an extremely hard nitride of iron (Fe_2N), which appears in the form of needles, and yields a structure not unlike that of a coarse martensite. The best results are apparently only obtained with steels containing about 1 per cent of aluminium, and there is thus the possibility of the formation of an aluminium nitride in addition to the nitride of iron. In ordinary steels which have been nitrided, the surface layers, although hard, are much too brittle to be of much practical use, but with steels containing chromium, vanadium, titanium, &c., a deeper and much less brittle case may be obtained. The carbon content of a steel which is to be nitrided is of considerable importance, since some carbon is lost during the process, and in order that the requisite strength in the core may be retained, these steels must have a much higher carbon content than ordinary case-hardening steels. *Nitralloy* steels, which are now manufactured under a patent licence, have the following compositions:

C.	Si.	Mn.	Cr.	Al.	Mo.	Ni.
0·38–0·43	0·2–0·3	0·4–0·6	1·6–1·8	0·8–1·25	0·15–0·25	0·3–0·6

The temperatures employed in nitriding are generally between 450° and 500° C., and no further heat-treatment is necessary. Since the whole process is carried out at temperatures much below the lowest critical point, no grain growth occurs, and the treatment is so simple that distortion is reduced to an absolute minimum.

The depth of case is usually less than 1 mm., even when a temperature of 500° C. is maintained for as long as 100 hours. This temperature must not be exceeded, however, if the best results are to be obtained.

The most satisfactory results are obtained by subjecting the steel to a heat-treatment operation before it is nitrided. This treatment consists in heating to 900° C., quenching in oil, and then tempering at about 600° C. The nitriding treatment which follows has no influence on the structure of the core, and the latter has the following test values:

> M.S.: 55–65 tons per sq. in.
> Elongation: 17–20 per cent.
> Impact: 30–40 ft.-lb.

It is interesting to note that the nitriding process is now being applied to certain of the austenitic steels, such as those employed for aero-engine valves, and with marked beneficial results.

Stainless or Rust-resisting Steels

Corrosion.

The protection of metals against corrosion constitutes one of the most difficult engineering problems, and some of the factors affecting corrosion will therefore first be considered.

It is now generally recognized that the process of corrosion is electro-chemical in nature, and involves an anode and a cathode in contact with an electrolyte. The fact that a mild steel will rust much more readily than pure iron has been known for a very long time. This can be accounted for by the fact that the ferrite and the pearlite areas in the steel, in contact with natural waters, give rise to a series of short-circuited electrolytic cells, the ferrite areas which constitute the anodes being rapidly attacked by the corroding medium. It is thus natural to infer that the homogeneity in structure of a metal has a pronounced influence on its corrosion-resisting properties, and a metal both chemically and physically homogeneous does indeed resist corrosion to a very remarkable extent. Chemically pure metals are very difficult to obtain, however, and in the commercial metals even small quantities of impurities tend to initiate corrosion to a very marked extent. Thus "Armco" iron resists corrosion much better than ordinary wrought iron, since it contains a lesser proportion of impurities.

Physical heterogeneity in a chemically homogeneous metal may also give rise to corrosion. For instance, cold-worked metals have a higher potential energy than unworked metals, and are therefore anodic to the latter. If a pure iron wire is cold-worked at one end and then immersed in salt water, the cold-worked end is rapidly corroded. Corrosion is often noticed around holes which have been punched in sheets and plates of metal, and the effect may occur even in the so-called stainless steels and alloys. For this reason, some firms insist that holes in plates shall be drilled or reamered. Welded joints, not only with different metals but of

the same material, may be attacked long before the main metal, owing to the difference in structure of the welded and unwelded parts, a consequence of the extremely high and localized temperature to which the actual weld is raised.   For this reason, the normalizing of welded steel parts is to be advised if such treatment does not materially influence the other physical properties.

The Rusting of Iron and other Metals.

Iron, if immersed in some corroding medium such as salt water, corrodes by dissolving to yield a ferrous salt with the liberation of hydrogen.   The ferrous iron is then oxidized by dissolved atmospheric oxygen with the formation of a hydrated ferric oxide or " rust ".   It might be expected, therefore, in a sheet of iron unevenly corroded, that the parts which are in closest proximity to the atmosphere would be corroded to the greatest extent.   That this is not so is readily demonstrated by examining the effect of a drop of salt water placed on a flat iron sheet, when it will be observed that round the edge of the drop where the oxygen concentration must necessarily be greater than in the interior, the iron remains uncorroded, whereas in the centre or " unaerated " part of the drop corrosion rapidly occurs.   Under such circumstances, corrosion is due to a difference in oxygen concentration in the liquid, and Evans has definitely shown that this " differential aeration " gives rise to differences in potential in the liquid with the consequent development of minute electric currents.   Corrosion thus occurs; but whilst the more aerated parts of a metal immersed in the liquid suffer cathodic protection, the unaerated parts become anodic and are corroded.   Thus if two sheets of the same steel are immersed in salt water and connected together, and if oxygen is bubbled over the surface of one sheet but not over the other, a current of electricity will flow so long as oxygen is supplied, the necessary energy being derived from the corrosion of the sheet which has been " screened " from the oxygen.   This applies to all metals which corrode, the anodic or " unaerated " parts always being attacked; i.e. those parts which are most inaccessible to oxygen are corroded first.   On this account, also, corrosion may be localized where parts of a metallic surface are screened from oxygen by contact with other substances which are chemically inert.   Thus Bengough has shown that particles of sand in contact with the surfaces of brass condenser tubes will initiate corrosion.

(E 428)   **12**

Any imperfection, such as a crack or pore, a tool or deep file mark on the surface of an otherwise homogeneous metal, may therefore initiate corrosion when it is immersed in some corroding medium, since at the base of such cavities the metal becomes anodic to the remainder of the surface, with a consequent enlargement and deepening of the original cavities. A smooth, highly finished surface is thus essential if the maximum resistance to corrosion is to be obtained.

The fact that some metals corrode more readily than others is well known. Aluminium and copper resist atmospheric corrosion to a very marked degree, and in both cases the comparative freedom from corrosion is attributed to the formation of an oxygen-containing oxide film on the surface, which protects the metal underneath from any further attack. Pure copper will retain its colour and appearance for a long time in a comparatively pure country atmosphere, but rapidly becomes tarnished in an atmosphere containing sulphuretted hydrogen, such as that in industrial districts. In such circumstances, however, the resistance to tarnishing is greatly increased by heating the copper to a temperature of about 70° C., a treatment which has no apparent effect on its colour or appearance. It is assumed, however, that the surface is covered with a very thin film of oxide, which then acts as a shield against further attack by the sulphurous gases present in the atmosphere.

The resistance of aluminium to corrosion is remarkable in view of the fact that normally it is a very reactive element, and the immunity of the aluminium alloys from corrosion is undoubtedly due to the presence of a thin protective film of aluminium hydroxide. Alloys of the duralumin type are now subjected to some treatment whereby this natural film is replaced by a thicker strongly adherent film. Mott first indicated that such a film could be formed by making the metal the anode in a bath of sodium phosphate, but Bengough and Sutton * have shown that better results are obtained by carrying out the anodic oxidation in a bath containing chromic acid. The process is essentially as follows: after thorough cleaning of its surface, the aluminium or its alloy is immersed in a solution of chromic acid along with a carbon rod; a small external E.M.F. is then applied so as to make the carbon the cathode and the aluminium the anode. The applied E.M.F. is then gradually increased to a value which, for duralumin, is about 50 volts. After

* Paper read before British Association, 1926.

being treated for some time in this manner, the surface of the metal becomes covered with a uniform glassy adherent coating of aluminium oxide, which also contains some oxide of chromium. This treatment greatly increases the resistance to corrosion by sea-water, and is now commercially applied to the light aluminium alloys employed in seaplane construction.

Passivity.

Faraday observed that concentrated nitric acid had apparently no action on iron and steel, due to a state described as passivity; and he concluded that this was due to the formation of a very thin protective coating on the metal. It is only comparatively recently that the actual existence of these passive films has been definitely established by Evans during the course of a series of masterly researches on the causes and prevention of corrosion. Nitric acid apparently favours passivity to a very pronounced extent, and the metal chromium when immersed in nitric acid becomes passive to a greater degree than iron, so much so that dilute solutions of nitric acid, which readily dissolve iron, have practically no effect on chromium. It is therefore not surprising to find that the iron-chromium alloys resist corrosion and attack by nitric acid to a very marked degree. In this connexion, however, it is necessary to consider the mode of occurrence of chromium in steels containing carbon. As indicated on p. 120, in low-percentage chromium steels the element is associated with both carbon and iron to form a complex carbide, without influencing the nature of the ferrite in the unhardened steels. When the chromium is increased beyond that required to form the double carbide, the excess exists in solid solution in the iron yielding a chromiferous ferrite, and it is only when this occurs that the steels show any marked resistance to corrosion; consequently, the so-called stainless steels must necessarily contain high proportions of chromium. Further, it will be evident that the higher the carbon content of the steel the higher must be the chromium, if the material is to exhibit satisfactory resistance to corrosion. Thus, whilst a stainless steel requires at least 13–14 per cent chromium, complete immunity from attack by nitric acid, atmospheric oxidation, and many organic acids can be obtained with a much lower chromium content in the " stainless irons " having a much lower carbon content. Again, when the carbon is sufficiently low in value, practically the whole of the chromium is in solid solution in the iron, and the structure of the

alloy is essentially homogeneous, even in the normalized condition; and for some purposes no further treatment may be necessary. On the other hand, the structure of an annealed or normalized stainless steel is heterogeneous, and this heterogeneity must be overcome by subjecting the material to a hardening operation which induces homogeneity and the consequent maximum resistance to corroding influences.

Stainless Steels.

These were discovered by Brearley in 1913, and although they were primarily developed for the manufacture of table cutlery, have since been applied to a great variety of purposes where resistance to corrosion is desired. In addition, these steels have formed the basis for the development of the modern heat-resisting steels which possess a truly unique combination of other physical properties.

Stainless steel for cutlery contains from 0·3 to 0·35 per cent carbon with 12–14 per cent chromium, and is therefore of about eutectoid composition (p. 120). It might be expected, therefore, by analogy with a plain carbon eutectoid steel, that the change from pearlite to austenite on heating would occur at a constant temperature. The change, however, is rather sluggish, and actually takes place over a considerable temperature range. No change occurs until about 800° C. is attained, and complete solution of the carbide does not result until a temperature between 900° and 950° C. is reached. Consequently, the latter temperature must be employed in hardening if the desired hardness and maximum resistance to corrosion are to be obtained (fig. 132 (a), (b), and (c)). A correctly hardened steel of this type consists entirely of martensite, and in view of its pronounced air-hardening tendency, the material can be obtained in this condition, if the section be not too massive, by quenching in oil, or in the case of very thin sections, by simply cooling in air. For cutlery, the steel is generally tempered below 250° C. immediately after hardening, in order to relieve hardening stresses; but for many engineering purposes, a higher tempering temperature must be employed in order to induce toughness and resistance to shock. Tempering below 500° C. has very little influence on the hardness of hardened stainless steel, as will be evident from the curve shown in fig. 133. In many cases tempering between 600° and 700° C. is recommended. This treatment somewhat decreases the resistance of the steel to corrosion, although
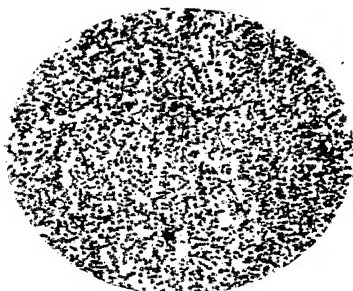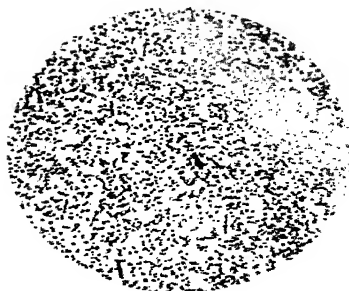
(a) × 500   (b) × 500

Fig. 132.—Stainless steel containing 0·41 per cent C, 13·7 per cent Cr. (a) Annealed: Vickers diamond hardness 250. (b) Oil-quenched 920° C.: Vickers hardness 525. (c) Oil-quenched 960° C.: Vickers hardness 642.
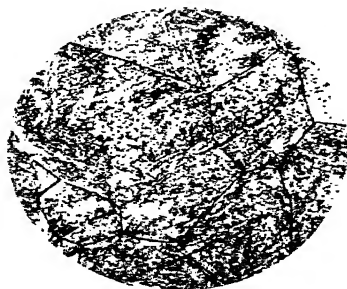
Fig. 134.—Overheated structure in stainless steel containing 0·4 per cent C, 14 per cent Cr. × 200. Note the evidence of excessive grain growth in the austenite during reheating.

its resistance to attack by air, water, sea-water, steam, nitric and organic acids is still very strongly marked. In this condition, the material can be readily machined, and the following test results are fairly representative:

Y.P.	M.S.	Elongation.	Reduction of Area.	Impact.	Brinell No.
50–60 tons	60–70 tons	15–20%	40–50%	15–25 ft.-lb.	225–321

Such a steel is most suitable for pump parts, pistons, impellers, valves and valve springs, turbine blades, &c.

The carbon content of this class of steel is generally not less than 0·35 per cent but not greater than 0·55 per cent. The steels containing more than 0·3 per cent carbon behave in much the same manner as the hyper-eutectoid plain carbon steels so far as heat-treatment is con-
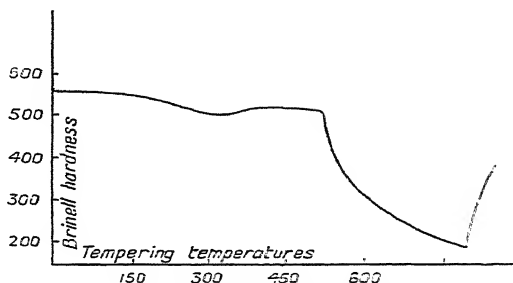
Fig. 133.—Curve showing the Effect of Tempering on the Hardness of a typical Stainless Steel quenched in Oil from 960° C.

cerned, in that much higher temperatures are necessary to obtain complete solution of the excess carbide which, in a stainless steel, is essential for the maximum power of resistance to corrosion. Further, the higher the carbon content the greater are the difficulties encountered in fabrication.

It has already been mentioned that the chromium raises the critical points in a stainless steel, and that a temperature between 900° and 950° C. must be employed in hardening. The effect on the microstructure of quenching at too low a temperature has been illustrated in fig. 132 (b). Such a steel would be lacking in the necessary tensile strength even after tempering, and in addition its corrosion-resisting properties would be seriously impaired. At the same time, however, it should not for one moment be assumed that a stainless steel cannot be overheated. Thus, fig. 134 is a section of a steel which showed excessive brittleness, and which had been drastically overheated, as evidenced by the coarseness of the martensite and the very large crystal grains. In such a structure

as this, the crystal boundaries are to be regarded more in the nature of intercrystalline cracks, thus accounting for the extreme brittleness of the material.

When the carbon content is below 0·15 per cent, the alloys are known as stainless irons. It must be realized, however, that these alloys contain a much greater proportion of pearlite in the annealed state than plain carbon irons of similar carbon contents, and it is therefore not surprising to learn that the properties of a stainless iron may be very considerably modified by heat-treatment, although, of course, to a lesser extent than the higher carbon stainless steels. Thus, an alloy containing 0·05–0·1 per cent carbon and about 13 per cent chromium, when quenched in oil from about 940° C., will give the following mechanical tests:

M.S., tons.	Elongation, per cent.	Reduction of Area, per cent.	Impact, ft.-lb.	Brinell No.
65–75	10–15	30–40	30–35	262–351
50–60	12–18		60–70	217–241—Td. 600° C.

In the soft (annealed) state, the Brinell hardness values are about 134–166. The above tests are influenced by the chromium content of the alloy. Thus, with increasing chromium content, the difference in the hardness between the annealed and quenched specimens becomes much less marked, until with about 0·1 per cent carbon and 17–18 per cent chromium the difference is very little indeed, and even in the quenched condition a Brinell number less than 250 may be obtained. Such steels are, however, extremely ductile and can be readily cold-worked, their hardness and tensile strengths being considerably increased thereby.

The Welding of Stainless Steel and Iron.

The high chromium steels can be readily welded either by the oxy-acetylene flame or the electric arc. Since resistance to corrosion is always a primary consideration in these steels, it is obvious that the actual weld should have a composition similar to that of the parts which are to be joined together. Thus, special welding metals are supplied by the steel-maker; but since these cannot be expected to have identically the same composition as the steel, the quantity of metal used in welding should be cut down to a minimum. More complete diffusion then occurs between the welded portions on subsequent heating, and in consequence the material is much more homogeneous in the vicinity of the weld and resists corrosion to a greater extent. If the weld is allowed

to cool too quickly, the heated parts may crack as a result of the air-hardening properties of the steel. The weakest part of a weld does not generally occur in the actual weld itself, but in those parts immediately on either side of it. In these areas, excessive grain growth may occur owing to the very high temperatures to which they are raised, and the fact that diffusion does not penetrate so far. This effect is illustrated in fig. 135, a particularly bad example of welding; and in this case the material was much too brittle as a result of the coarse heterogeneous nature of the material in this region, which again emphasizes the necessity for an annealing or normalizing treatment after welding. Reheating will also tend to destroy the cored (cast) structure that may exist in the actual welded portion.

Influence of other Elements on the Properties of Stainless Steel and Iron

Silicon.—This element may be present in considerable quantity in the high chromium steels because the alloys used in manufacture often contain much silicon. For most engineering purposes the silicon should be kept below 0·5 per cent, since although higher proportions cause slightly better resistance to corrosion, particularly as regards attack by dilute sulphuric acid, they result in a drastic lowering of the tensile strength, ductility, and resistance to shock. High silicon also increases the difficulty in the forging of thin sections. However, steels containing about 3 per cent silicon and up to 0·55 per cent carbon, but a much lower chromium content (up to 9 per cent), are frequently employed in the manufacture of valves. These steels resist oxidation at high temperatures to a very pronounced extent, and since the critical temperatures are usually much higher than those to which the articles are raised in actual use, they do not " airharden " to any appreciable extent as a result of the variations in temperature to which they are subjected. The effect of silicon in raising the critical temperatures in stainless steel must, of course, be taken into consideration in heat-treatment, and a hardening temperature of at least 1000° C. should be employed, a treatment which is generally followed by tempering at about 800°–850° C.

The following tests are typical of such materials in the heat-treated condition:

Y.P.	M.S.	Elongation.	Reduction of Area.
45–55 tons	55–65 tons	15–20%	35–50%

Nickel.—Nickel may be found in many stainless steels in quantities up to 2 per cent, but is then to be regarded as an accidental rather than an essential constituent. Small proportions of nickel do not appear to have much influence on the properties of the steel beyond lowering the critical points, and therefore the temperatures necessary for hardening. Much higher proportions, however, result in a very marked alteration in the properties of the steel. In the first place, the alloys are almost entirely austenitic even with ordinary rates of cooling, the nickel bringing about a great depression of the critical points. The materials are not so susceptible to heat-treatment as an ordinary stainless steel, and are only obtained in the softest condition by quenching from about 1100° C. In this condition the steels are extremely tough but very ductile, and are readily cold-worked. A high carbon content seriously minimizes the capacity for cold-work, and for this reason the element is usually kept as low as possible. The austenitic nickel-chrome steels resist attack by acids and corrosion generally, both at ordinary and elevated temperatures, to a much greater extent than ordinary low-nickel stainless steels. Well-known alloys of this class are sold under the trade names " Anka " (Messrs. Brown, Bayley's Ltd.), " Staybrite " (Messrs. Thos. Firth & Sons Ltd.), and " V.2.A. " (Messrs. Fried. Krupp, Germany); and the development and applications of these alloys are largely due to the researches carried out by the firms mentioned. The compositions vary, but are generally between 15 and 20 per cent chromium and 10–7 per cent nickel, the higher chromium being associated with the lower nickel content.

Tungsten and molybdenum are sometimes added to these alloys, either element apparently conferring enhanced resistance to corrosion by acids. Such materials have thus found considerable application in large chemical plant.

The truly austenitic alloys can only be hardened by cold-work, the effect of which is then only overcome and the material softened by reheating and quenching from 1000° to 1100° C.

Typical microstructures for a steel of this class are shown in fig. 136, from which it will be observed that the austenite behaves

Fig. 135.—Showing structure of welded stainless iron sheet in the vicinity of the weld.   × 35 but reduced in reproduction

(a) × 200
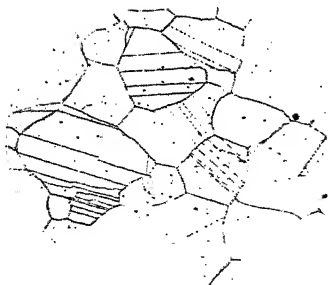
(b) × 200
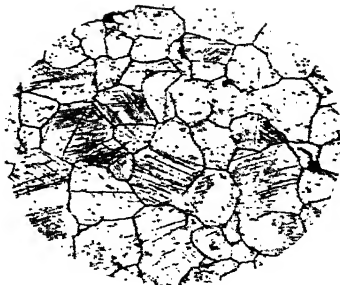
(c) × 200

Fig. 136.—Microstructures of a steel containing 0·1 per cent C; 0·69 per cent Si; 0·3 per cent Mn; 18·09 per cent Cr; 9·12 per cent Ni. (a) As rolled: Vickers hardness 292. (b) Softened by reheating to 1150° C. and cooling in air. Note the twinned crystals. Vickers hardness 160. (c) As (b) but cold-drawn: the strain lines in several austenite crystals are clearly marked. Vickers hardness 307.

as a true solid solution in that cold-working results in the formation of strain lines or lamellæ, whereas working followed by annealing leads to the production of twinned crystals, features which serve to indicate the treatment to which the alloy has been subjected. The hardening effect of cold-work is evident from the Vickers hardness numerals given.

In the softened condition these steels are non-magnetic, and the following test results, due to Hatfield, may be accepted as typical:

Y.P.	M.S.	Elongation.	Reduction of Area.	Impact.
13–20 tons	37–53 tons	55–71%	58–68%	84–110 ft.-lb.

Austenitic nickel-chromium-iron alloys of this type become relatively brittle at temperatures between 700° and 800° C., and should not, therefore, be worked in this temperature range. The materials are also liable to intercrystalline corrosion after they have been heated to temperatures between 650° and 900° C. This effect is of obvious importance in connexion with welded parts in which maximum corrosion occurs on either side of, although at a considerable distance away from, the actual weld. The only remedy consists in normalizing or quenching the welded material from a temperature of about 1050° C.

The Influence of Temperature on the Properties of Steel

Heat-resisting Alloys.

Tests carried out in the ordinary manner at normal temperatures are of little or no value in indicating the behaviour of a steel at very low or at elevated temperatures. This will be evident from the curve given in fig. 137, due to Desch, which has been plotted from data obtained by several workers, since it has been shown that the curves for mild and medium carbon steels are of sensibly the same form. The dotted portions of the curve were obtained by extra- and inter-polation, and not from experimental data.

Considering low temperatures first, it will be observed that the tensile strength of iron at temperatures below 0° C. increases rapidly with falling temperature from about 22 to about 60 tons per square inch at absolute zero. As might be expected, this increase in tensile strength is accompanied by increased brittle-

ness, as measured by the ordinary notched bar test; and all carbon steels exhibit a rapid falling off in impact values as the temperature is lowered. It is of interest to note that the nickel steels are affected to a much lesser extent, and consequently the impact-temperature curves for temperatures below 0° C. are much flatter.

The influence of low temperatures on the properties of iron and steel is of extreme importance when the materials are used in the colder regions of the world, and also when they are employed in refrigerating machinery.

Some information respecting the properties of steel at high temperatures is of primary importance to the engineer in view of the modern tendency for the employment of higher temperatures and pressures such as those met with in steam-engine plants, internal-combustion engines, &c. The influence of elevated temperatures on the properties of several steels differing greatly in composition are illustrated by the curves in fig. 138, which have been plotted from data obtained by Hatfield.*

Fig. 137.—Curve showing Variation in Tensile Strength with Temperature of Iron almost free from Carbon

The first important feature brought out by the above curves is the fact that a steel does not necessarily possess its greatest strength at ordinary temperatures, but that in most cases the curve exhibits a well-defined maximum value, which, for ordinary medium and low carbon steels occurs between 250° and 350° C. This increase in strength is accompanied by a marked lowering in the ductility values, and in particular the resistance to shock. Even dead-mild steels exhibit this phenomenon, and to it the term *blue-brittleness* has been applied, in view of the fact that it occurs at temperatures corresponding to those which are necessary

to produce blue tints on the surface of polished carbon steel.

The true explanation of blue-brittleness has not yet been given, but it is obvious that a steel should not be worked within the " blue " range of temperature. For this reason, boiler and ship plates should be heated to a temperature above the " blue " region before being bent, otherwise the material may rupture, and in
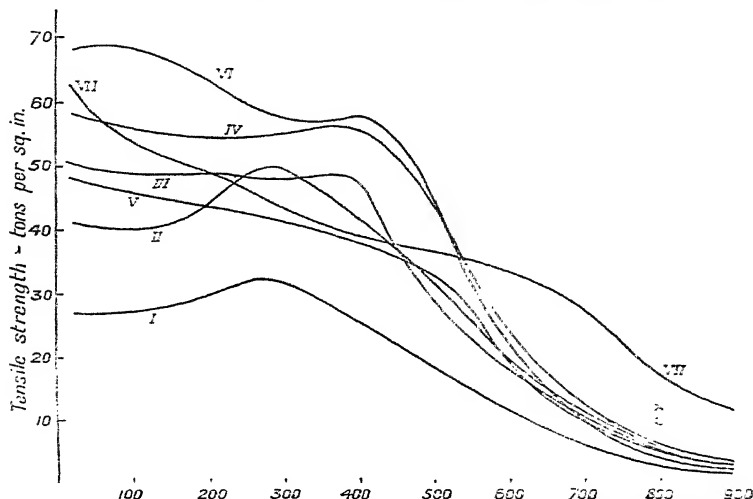
Fig. 138.—Curves showing Effect of Temperature on Strengths of various Steels (Hatfield)

    I. 0·14°/₀ C steel—normalized.
    II. 0·42°/₀ C steel—normalized.
    III. 0·32°/₀ C : 3·07°/₀ Ni—O.Q. 850° C.; Td. 630° C.
    IV. 0·29°/₀ C : 0·89°/₀ Cr : 3·41°/₀ Ni—O.Q. 830° C.; O.Q. 600° C.
    V. 0·27°/₀ C : 13·3°/₀ Cr—O.Q. 950° C.; Td. 760° C.
    VI. 0·6°/₀ C : 3·98°/₀ Si : 8·75°/₀ Cr—O.Q. 1075° C.; Td. 900° C.
    VII. 0·4°/₀ C : 13·65°/₀ Cr : 10·31°/₀ Ni : 3·53°/₀ W—A.C. 950° C.
    ⊗ H.S. steel—0·54°/₀ C : 4·08°/₀ Cr : 18·0°/₀ W : 0·84°/₀ V—annealed
    × Valve steel—1·51°/₀ C : 13·22°/₀ Cr : 1·08°/₀ Ni : 5·17°/₀ Co—softened.

riveting it is important that the rivets should not be hammered below a dull red heat or they may crack and the heads break off.

The curves in fig. 138 also show that the strengths of all the steels, with the exception of VII, are exceedingly low at high temperatures. Thus a load of only 2 tons per square inch is sufficient to fracture a 0·14 per cent carbon steel at 900° C. It will be observed that the introduction of either chromium or nickel does not materially affect the properties of a steel above 550° C., but that

the best results are obtained by a suitable combination of nickel and chromium with tungsten. With steels of this description, tensile strengths of between 20 and 25 tons per square inch at 900° C. may be obtained, and the following results, due to Hatfield, may be regarded as typical:

Composition.						At 15° C.		At 800° C.		
C.	Si.	Mn.	Cr.	Ni.	W.	M.S.	Elonga-tion.	M.S.	Elonga-tion.	Reduction of Area.
0·42	0·69	0·31	13·30	8·87	3·42	56·8	7·5%	22·75	16·0%	32·8%

These steels are truly austenitic and cannot be hardened except by cold-work, and in order to soften them the materials are reheated to 1100°–1150° C. and cooled in air.

Such steels are now extensively employed for the manufacture of aero-engine valves, and are often case-hardened by means of nitrogen before being placed into service.

In many instances resistance to oxidation (scaling) and attack by various gases at high temperatures are equally as important as the tensile strength; and in this connexion, also, the high nickel high chromium alloys give most satisfactory results, although the best resistance to oxidation and scaling is apparently only obtained when a fair quantity of silicon is present also. In some of the alloys which have found considerable application in both mechanical and chemical engineering, this element may be as high as 1·5 per cent. Molybdenum has also been introduced into some of the Ni-Cr-W-Si alloys used for exhaust valves, the element apparently conferring enhanced resistance to oxidation and scaling, as well as increasing the strength and impact values at high temperatures.

Creep.

At ordinary temperatures, the rate of loading does not materially influence the results obtained by the ordinary tensile test. At higher temperatures, however, this rate becomes of paramount importance, since, as Dickenson has shown,* a test-piece will break at a much less load than the maximum stress as ordinarily determined, provided that sufficient time is allowed for plastic flow to occur. The gradual extension of such a heated specimen with time when under the influence of a constant load constitutes what is known as " creep ", and recognition of this phenomenon

* *J.I.S.I.*, 1922 (ii).

is of the utmost importance in connexion with metals working at elevated temperatures. Dickenson's original work has since been taken up and extended by several workers, whose results have confirmed the hypothesis postulated by Lea, that "for a metal (say, a steel) of given composition, there exists at each temperature a stress which, if exceeded, will cause continuous creep, and in time will result in the fracture of the stressed part". This stress is known as the "limiting creep stress", and must therefore not be exceeded if a material is to assume any permanence of dimensions at a given temperature. At ordinary temperatures the limiting creep stress for metals is not very different from the ordinary maximum stress, but as the temperature rises the limiting creep stress may become but a very small fraction of the ultimate tensile strength as determined in the ordinary manner. This will be evident from the following data, due to Batson, the result of investigations carried out at the National Physical Laboratory:

| Temperature. | Steel for Boiler and Superheater Tubes. | | | | Carbon Steel for Superheater and Steam Drums. | |
| | 0·10 per cent C. | | 0·17 per cent C. | | 0·23 per cent. | |
	M.S.	Limiting Creep Stress, tons.	M.S.	Limiting Creep Stress, tons.	M.S.	Limiting Creep Stress, tons.
400° C.			29·0	13·4	26·0	13·5
470° C.					18·5	7·0
480° C.	17·0	5·5	21·5	6·0		
500° C.	14·9	3·5	19·4	4·8		
525° C.	13·7	2·0	17·0	3·5		
530° C.					16·4	4·0
550° C.	12·1	1·3	15·0	2·4		
570° C.	10·5	1·0	13·0	2·0		
600° C.	8·4	0·6	11·0	1·2		

The very serious falling off in the limiting creep stress values with increase in temperature is at once evident, and this must obviously be considered in connexion with metals working under stress at high temperatures, such as are employed in boilers, superheaters, internal-combustion engines, &c., and in such cases the safe working stress is below the limiting creep stress. According to Lea, the limiting creep stress for copper alloys rapidly decreases above 250° C., and for carbon steels containing not more than 0·45 per cent of carbon it is considered that the maximum safe temperature for vessels to withstand internal pressure is not much above 500° C. Assuming that the limiting creep stress is the stress with which the working stresses should be compared in order to arrive at the factor of safety, a simple calculation using the values

given in the above table will show that an increase in the working temperature is of much more serious import than a corresponding percentage increase in the actual working stresses.

Much work remains to be done on the determinations of the limiting creep values for all classes of steel, but it is interesting to note that the Ni-Cr-W steels yield relatively high values, which, together with their non-scaling and non-corroding properties, will probably lead to their more general application for vessels working under pressure at temperatures above 500° C.

It should be mentioned that neither the limit of proportionality nor the yield-point gives any indication of the limiting creep stress, and the latter may be higher or lower at some given temperature than either of the other values. Further, although the heat-resisting Ni-Cr-W steels may give lower values for the yield-point than, say, those of a heat-treated nickel-chrome steel, much higher values for the limiting creep stress are obtained.

At the present time there exists some difficulty in definitely fixing the point at which creep ceases, since it has been suggested that this may occur so slowly that years may be necessary to give any indication on the extensometers at present in use. In order to arrive at the practical limiting creep stress, it is usual to plot the extension against time when the specimen is subjected to a constant load and at constant temperature. If the stress is below the limiting creep stress, the curve gradually rises, but after a time, which may be several months, it becomes flat and parallel to the axis of time: the greatest value of stress yielding a curve of this type is then taken as the limiting creep stress. The types of curves obtained are illustrated in fig. 139, the result of experiments carried out by Lea on cupro-nickel.[*] From the figure it is evident that the limiting creep stress is between 6 and 7 tons per square inch at 300° C. Above the limiting creep stress, the creep-time curve for steels is of the same general form as that shown.

It will be evident that the determination of the limiting creep stress involves a considerable number of observations taken over a comparatively long period of time, and in order that some practical information with regard to stability of dimensions may be obtained in a reasonably short time, Hatfield has recently introduced what he describes as the " time-yield " value.[†] This is obtained by loading the specimen statically, and is the stress

within which, at a given temperature, stability of dimensions is obtained within a period of 24 hours for a further period of 48 hours, with an extension not exceeding the elastic deformation of 0·5 per cent on the gauge length, and with limitation as regards measurement for permanence of dimensions of the order of one millionth of an inch per inch per hour. Hatfield considers that
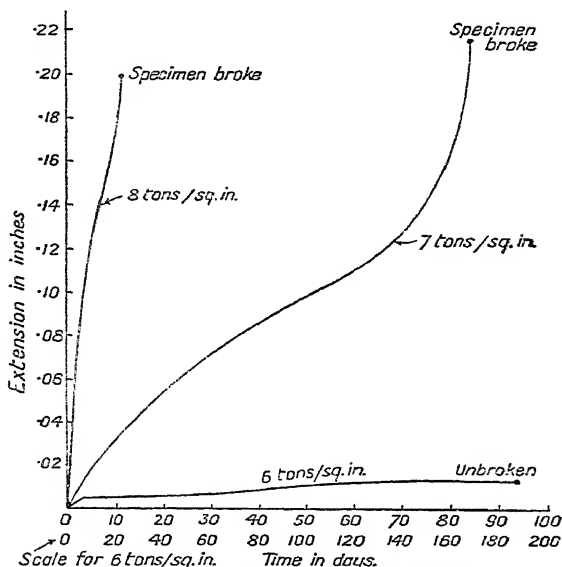
Fig. 139.—Creep-time Curves for Cupro-nickel (Lea) at 300° C.

two-thirds of this time-yield value may be taken as the " safe stress ", and this is now being used by some engineers. The time-yield values for various steels are placed in a similar order to those obtained for the limiting creep stresses, although the two values at any given temperature differ considerably at temperatures below 500° C. Above this temperature, however, the two values are almost identical, and it is thus evident that at such temperatures Hatfield's time-yield values may be accepted by the engineer as a basis for design.

The Cold-working of Metals

The facility with which some metals can be deformed when cold by pressing, hammering, rolling, and drawing constitutes one of their most useful properties.

At ordinary temperatures the application of a stress which is less than a certain limiting value merely results in elastic deformation, and the metal resumes its original shape and dimensions when the stress is removed. When this stress, known as the elastic limit, is exceeded, plastic deformation takes place, and the material no longer returns to its original shape upon removal of the stress. The effect of a unidirectional stress is to distort the crystal grains in the direction in which the stress is applied. At one time it was thought that plastic deformation in metals occurred in a manner similar to that which occurs when a very viscous substance such as soft pitch is deformed. The true mechanism of deformation in metals is only satisfactorily explained by the " slip " theory of Ewing and Rosenhain, and the " vitreous " or " amorphous " theory of Beilby and Rosenhain. The former theory assumes that, during plastic deformation, slipping of adjacent parts of the same crystal takes place along crystallographic or cleavage planes. The amorphous theory goes further and assumes that this slip results in the destruction of the crystalline arrangement of the atoms lying in and about those planes. It is further assumed that during the process of slipping the intensely localized pressure in such planes actually causes momentary liquefaction, but that the liquid is so quickly chilled that it is unable to recrystallize, and is thus retained in a non-crystalline or amorphous form. This substance is known as *amorphous cement*, since it acts as a binding material holding adjacent crystalline parts together.

When, within a crystal, slip first occurs, the liquid layer, which is but a few atoms in thickness, acts as a lubricant. The relative movement of parts then results in a local release of this pressure and the solidification of the liquid. The amorphous phase is stronger than the crystalline material, and hence further slip in its immediate neighbourhood is inhibited. Since even a very small piece of metal may consist of an enormous number of crystals of varying orientations, it is evident that in some of them the gliding planes will be so situated that slip will most readily occur under the influence of a given unidirectional stress, whilst other crystals

will be so orientated that slip does not occur in them to any appreciable extent. As the stress is increased, the strong amorphous phase is developed along planes in certain crystals, and this throws additional stress on to the surrounding crystals, with the consequence that slip occurs in them also. The material thus continues to deform until fracture finally occurs.

Some proof of the above hypothesis is given by the micro-examination of the polished surfaces of metals which have been permanently deformed. A series of dark bands, known as *slip-bands*, are then often observed. Slip-bands cannot be seen on the surface of a specimen which is polished after being cold-worked, but instead a series of fine lines, known as *strain lines*, which generally change direction at each crystal boundary, are observed (figs. 136 (*c*) and 158, pp. 180 and 216). The presence of these lines can thus be taken as evidence that the material has been cold-worked, but it should be noted that they may be induced in a specimen to a certain extent by such operations as heavy filing or sawing, which may be necessary in the preparation of the specimen for microscopic examination. In such cases the strain lines are generally confined to a few crystals only.

Cold-work increases the hardness of a metal, a fact which is readily explained by the above theory, since any amorphous material that is formed must necessarily exist in a form analogous to that of an undercooled liquid, and consequently possess a higher potential energy than the ordinary crystalline form. Further, such a substance must be regarded as being in a state of unstable equilibrium, and that this is so is evidenced by the fact that the hardness developed in a metal by cold-work is readily and completely removed by annealing at comparatively low temperatures. As the temperature rises, some of the crystals initially formed grow at the expense of others to yield a structure containing fewer but larger crystal grains. This recrystallization commences and is developed along the cleavage planes of the original crystals, with the consequence that, after cold-working and annealing, many metals exhibit banded structures known as " *twinned* " *crystals* (figs. 136 (*b*) and 159, pp. 180 and 216). Twinning thus affords distinct evidence that a metal has been cold-worked and subsequently annealed, and the size of the twinned crystals somewhat indicates the temperature which has been employed in annealing, although time exerts a not inconsiderable influence on crystal growth.

Incidentally, it may be noted that the fine-grained structures produced by hot-working are in all probability due to the simultaneous production and recrystallization of any amorphous material which may be formed during working. There is, however, a certain definite temperature depending on the metal itself, and also on the degree to which the material has been cold-worked, below which recrystallization does not occur; and if the metal is subjected to stress below this temperature, it becomes strain-hardened even though the temperature may be considerably higher than that of the atmosphere. Hence one reason for the normalizing and annealing of forged and rolled steels, since there is always the possibility that the material may have been finished at too low a temperature, with the consequent development of internal stresses which in all probability are unequally distributed.

From what has already been stated, it might be expected that pure metals and homogeneous solid solutions would be deformed to a much greater extent by cold-work than metals having a composite structure, since in the latter case the different constituents are not likely to suffer deformation to the same extent under the action of a given stress. A hard constituent will resist the stress, whereas a softer constituent may yield to the stress and flow, with the consequence that internal fissures or microscopical cracks readily develop at the bounding planes between them, and the metal soon fractures. Thus, although an alloy containing 70 per cent copper and 30 per cent zinc will undergo deformation to a very pronounced extent by cold-working, since it consists of one solid solution only, an alloy of copper with 40 per cent of zinc, which is composed of two solid solutions having widely differing physical properties, cannot be cold-worked to any appreciable degree.

Ordinary steels in the unhardened state are heterogeneous in nature, and, in most cases prior to cold-working, special treatments are carried out in order to obtain a fine microstructure which approximates as closely as possible to that of a homogeneous solid solution, in which are suspended particles of carbide of iron in the finest state of sub-division and most evenly distributed.

The two most important cold-working operations are: (a) cold-drawing for the production of rods and wire, and (b) cold-rolling for the production of sheets and strip. In addition, cold-pressing to shape is often carried out.

In almost every cold-working operation, the forces producing

deformation are essentially compressive forces. This is obvious in the case of cold-rolling, and in wire-drawing the compressional stress is applied by the circumferential pressure developed by passing the wire through a hole having a pronounced taper (fig. 140). The straight part of the hole serves to resist wear and leads to the production of a wire possessing a uniform cross-section and diameter.

The objects of cold-working are: (*a*) to shape the metal into a required form and size; (*b*) to obtain a smooth well-finished surface free from defects; and (*c*) to harden or " stiffen " the material. In some instances, hardness may not be desirable, and it is then necessary to subject the material to annealing treatments at various stages or at the end of the cold-working operations. In other cases (*a*) and (*b*) are the primary considerations, the effect of the cold-work on the mechanical properties being of little or no importance.

It will be remembered that in connexion with the heat-treatment of steel the production of coarse large-grained crystal structures is to be avoided, and the same applies to non-ferrous metals which are not cold-worked. On the contrary, if a metal

Fig. 140.—Section through Hole in Drawing Die with Wire passing through.

is to be cold-worked, the formation of comparatively large crystals is rather desirable than otherwise, since the material will then withstand deformation to a much greater degree than if it consisted of very small crystal grains. This can also be explained by means of the Beilby-Rosenhain hypothesis, since it is assumed that the crystal boundaries themselves are composed of the amorphous phase, which inhibits slip, and in a small-grained structure there are obviously many more of these boundaries than in a material containing larger but fewer crystals.

The Cold-working of Steel.

The raw materials for cold-rolled sheets and strip and cold-drawn steel wire are the hot-rolled sheets and wire-rods, and since in many instances the primary object of cold-working is to obtain a smooth surface on the finished material, it is important that the raw materials should also be free from surface defects. Fortunately for the engineer, defects in steel are readily revealed in the actual cold-working process

Acid-cleaning or " Pickling ".

Hot-rolled rods and sheets are covered with scale or oxide of iron, and before the material is subjected to cold-work this coating must be removed. This is accomplished by " pickling " the steel in acid. In addition to removing scale, pickling serves to reveal surface defects such as cracks, rokes, and laps, and is indeed often applied to steel bars and billets for this purpose alone.

At one time, solutions of vitriol in water containing about 5 per cent of actual sulphuric acid were commonly employed, steam being injected into the pickling tank in order to raise the temperature and accelerate the cleaning operation. The atmosphere in a pickling shop utilizing this method is almost unbearable, and, although still employed in some cases, vitriol has been largely superseded by commercial hydrochloric acid. This possesses the advantage that it can be used cold, and solutions containing about 7 per cent of the acid are generally used for carbon steels. Somewhat stronger solutions are necessary for alloy steels and for stainless iron and steel. Hatfield recommends a mixture of equal volumes of spirits of salt and water, to which a little nitric acid has been added.

At this point it is perhaps not out of place to mention the danger associated with the pickling of hardened steels. It must be remembered that a steel which has been hardened, particularly if the carbon content is high, is in a highly stressed condition, and, during pickling, the surface layers are dissolved so that the stress in adjacent layers is relieved, with the consequence that cracks are readily developed on the new surface. Such articles as hardened tools, magnets, &c., should therefore never be pickled, and if it is desired to clean the surface sand-blasting should be employed.

One other effect associated with pickling must be mentioned, that is, the development of brittleness in the steel after it has been immersed in the acid. This is attributable to the penetration and occlusion of the hydrogen gas which is generated by the action of the acid on the steel. This brittleness, although very real, is only temporary, and disappears entirely when the material is allowed to stand for several days, and much more rapidly when the steel is heated or " baked " at temperatures between 100° and 150° C.

Sutton * has stated that the brittleness induced by pickling is, in general, greatest when the steel is in its hardest condition and least when in the softest condition. Sutton has also shown that medium and high carbon steels when hardened and tempered at temperatures below 300° C., if subjected to deformation in this condition and then pickled, are liable to develop cracks at places where deformation has occurred. These cracks develop during pickling, and complete fracture may then ensue. The addition of certain organic compounds such as pyridine and quinoline, known as " restrainers ", to the pickling tank apparently diminishes pickling brittleness, and also promotes more uniform cleaning.

After pickling, wire or rod which is to be cold-drawn is well washed with water and then placed in lime in order to get rid of the last traces of acid and also to prevent rusting. The limed coils are then heated in ovens to about 150° C. The latter treatment removes pickling brittleness, and since the material is thoroughly dried most of the adherent lime can be shaken off quite readily. For sheets the liming operation is dispensed with, since there is the possibility that particles of lime may be rolled into the strip and then yield a poor surface.

Influence of various Factors on the Cold-drawing of Steel.

As the carbon content increases, the structure of steel becomes more heterogeneous in character, with the consequence that its capacity for withstanding cold-work also decreases. This is evident from the following data:

Original Size.	Carbon Content.	Reduction of Area of Cross-section drawn to Breaking Point.
0·252″ diam.	0·10%	96·0%
0·252″ ,,	0·50%	86·5%
0·252″ ,,	0·80%	66·0%

In actual practice, the extent to which deformation is carried out is considerably less than the figures given.

The necessary reduction in cross-section is not of course obtained in one operation, but the material is successively passed through several holes of decreasing diameter. The first pass, or " draught " as it is called, is regarded as the most critical, and therefore involves a much less reduction in cross-section than subsequent passes.

The tension on the wire in cold-drawing can generally be

safely taken to about 70 to 75 per cent of the ultimate breaking stress.

The speed at which the wires travel through the draw-plate, although somewhat dependent on the carbon content of the steel, is governed chiefly by the diameter. The higher the carbon content and the thicker the rod or wire, the slower will be the speed of drawing, the following data being quite typical:

Size.	Carbon Content.	Speed, ft. per min.
0 Gauge	0·80	104
3 Gauge	0·80	208
7 Gauge	0·80	250
0 Gauge	0·15	115
3 Gauge	0·15	250
7 Gauge	0·15	345

The structure of the steel exerts an all-important influence on its cold-drawing properties, and a correct structure must be induced in it before it is subjected to cold-work. With very mild steels, the fairly rapid rate at which the steel cools after being hot-worked yields a structure similar to that obtained by a true normalizing treatment, and this generally suffices.

Fig. 141.—Illustrating the Production of Incipient Flaws in Cold-drawn Wire

Medium and high carbon steels are more often subjected to a heat-treatment operation known as *patenting*. This consists in heating the steel to a temperature of about 1000° C. and then cooling in air, or better still in molten lead. As would be expected, the high temperature employed results in considerable grain growth, and since the sections are generally somewhat thin the cooling is fairly rapid, with the result that the microstructure consists of large grains of sorbite, and in the case of a medium carbon steel with free ferrite in the form of discontinuous crystal boundaries. Such structures withstand much more cold-work than material which has not been patented.

For correct wire-drawing, it is essential that the whole cross-section of the wire should pass through the hole in the draw-plate at a uniform rate, i.e. the outside layers should not flow at a greater or slower speed than the interior. If this uniform flow is not maintained a series of incipient flaws is developed in the interior of the wire (fig. 141), and eventually the material fractures. The commonest defect encountered is due to the outside layers

Fig. 142.—Section of wire which broke with cuppy fracture during drawing. × 200. Failure due to decarburization.

(a)

(b)   (c)
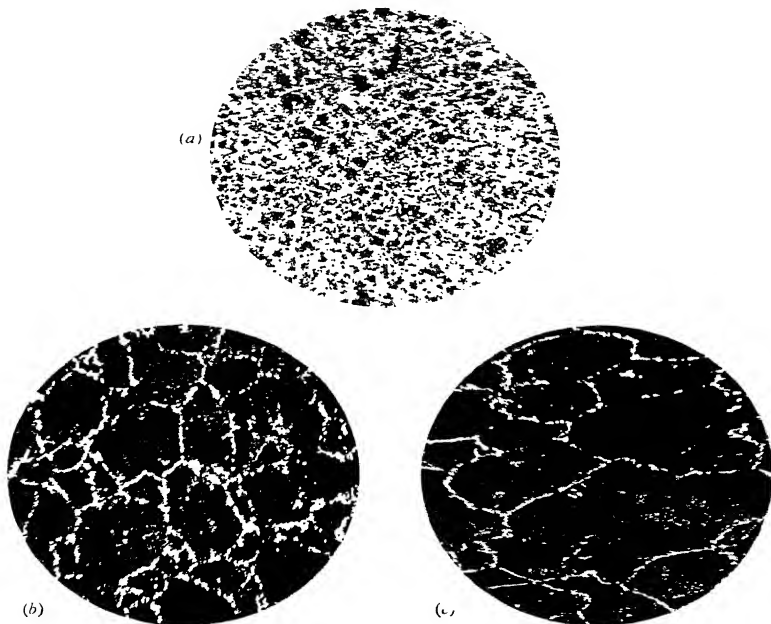
Fig. 143.—Micrographs of steel of the following composition: C, 0·4; Si, 0·144; Mn, 0·875; S, 0·046; P, 0·044

All the photographs are of longitudinal section and magnified 120 times.
(a) Hot-rolled rod. (b) After patenting. (c) After being cold-drawn.

flowing at a greater rate than the interior, i.e. the core lags behind the skin, and the wire generally fractures early on in the drawing operation with a very pronounced cup-and-cone fracture. Common causes of cuppy fractures are decarburization of the outer layers, and segregated centres such as may be met with in badly piped steels. The micro-photograph of a wire which failed owing to one of these causes is shown in fig. 142.

Other causes of fracture during cold-working are the formation of martensite in the outer layers owing to a very rapid rate of cooling during patenting, and the formation of coarsely laminated pearlite due to a very slow rate of cooling in normalizing. Again, if the time taken in patenting is not sufficient to yield a uniform temperature throughout, the crystal grains in the core may be considerably smaller than is desirable. The effects of patenting and drawing on the microstructures and mechanical tests are illustrated in fig. 143 and by the following data:

Condition.	Y.P., tons per sq. in.	M.S., tons per sq. in.	Elongation, per cent.	Reduction of Area, per cent.
(a) Hot-rolled, 0·252″ diam. ..	29·0	49·0	29·2	57·0
(b) After patenting	28·0	51·0	41·5	62·0
(c) After cold-drawing to 0·187″ diam., i.e. after 44 per cent reduction by cold-work ..	51·0	65·0	19·2	49·2

As the amount of cold-work increases, the tenacity values increase, but the elongation per cent, reduction of area per cent, and impact values are diminished, as will be observed from the following figures obtained for a steel containing 0·16 per cent carbon and 0·68 per cent manganese:

Condition.	Y.P., tons per sq. in.	M.S., tons per sq. in.	Elonga-tion (2″), per cent.	Reduction of Area, per cent.	Izod Im-pact, ft.-lb.
Hot-rolled, 0·464″ diam. ..	20·0	28·6	38·0	70·0	96
Cold-drawn to 0·429″ diam., i.e. after 13·5 per cent reduction	29·0	34·6	24·5	60·2	50
Cold-drawn to 0·403″ diam., i.e. after 24·5 per cent reduction	38·1	40·6	13·6	54·8	35

The above composition is that of a plain carbon case-hardening steel, and the cold-drawn bars possess certain advantages over those which are finished hot. Cold-drawn bars of uniform section are readily obtained and have a good smooth finish which often becomes part of the final product. Machining is then reduced to an absolute minimum, and the effects of cold-working do not influence the case-hardening properties of the steel, since

recrystallization occurs and is complete long before the temperature necessary for carburizing is attained.

Cold-drawn steels, on account of their uniform size, are particularly suitable for automatic machines where only very slight variations in size are permissible. At the same time, however, it should be indicated that the cutting of fine threads in the surface layers of cold-drawn bars which are not subjected to any further form of treatment may cause stripping, since it must be remembered that the surface layers are much harder than the interior, particularly after considerable reduction in cross-section. For threaded parts, where the only machining operation is that of screwing, better results are given from machined bars of much larger diameter.

Steels containing from 0·7 to 0·85 per cent of carbon are often cold-worked so as to yield a tensile strength of 110 to 120 tons per square inch, and the wires are then employed for wire-ropes, &c.; whilst for piano wires the steel is cold-worked until the material will withstand as much as 160 tons per square inch. The structure of such a wire before and after cold-working is shown in figs. 144 and 145, in which the fibrous or stratified appearance of the final product is clearly observable. In order to obtain such high tensile strengths, the steel is really severely cold-worked, and it is suggested that the treatment is too drastic since it lowers the resistance to shock to a greater extent than is desirable, and that a tensile strength of 85 to 95 tons per square inch should not be exceeded for such purposes as wire-ropes.

Influence of Tempering on the Properties of Cold-drawn Steels.

The curves given in fig. 146 may be regarded as typical. It will be observed that the curves for the maximum stress and yield-point show a distinct maximum at about 200° C., and that after 400° C. is reached these values fall rapidly. The elongation is slightly improved as the temperature is increased up to 400° C., but the values for the bend test, which for certain purposes is regarded as one of the most important tests applied to cold-worked materials, are lowered by tempering at temperatures up to 400° C., and satisfactory figures are not obtained until about 550° C. is reached. Another very important test not indicated by the diagram is the torsion or twisting test. This is carried out by twisting either a single wire, or two wires which are initially parallel, and
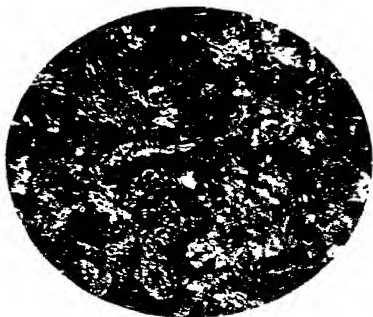
Fig. 144.—High carbon steel wire after
" patenting ". × 120

Fig. 145. — High carbon steel wire
patented and then cold-drawn to yield a
tensile strength of 100 to 110 tons per
sq. in. × 120.

Fig. 149.—Section of cold-rolled stainless steel
sheet (unetched) which was badly " rusted ", showing
particles of " rolled-in " scale. × 200.
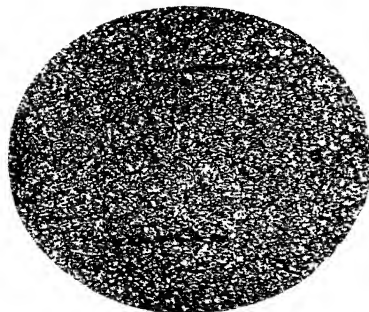
Fig. 151.—Cold-rolled alloy steel strip after
being hardened and tempered. × 350

Fig. 152.—Cold-rolled austenitic Ni-Cr-Fe
alloy sheet (carbon, 0·18 per cent; nickel, 8·7
per cent; chromium, 18·1 per cent). × 200.

counting the number of complete revolutions through 360° which are necessary to cause fracture.

The effect of tempering on the properties of cold-drawn steel is of importance in connexion with the operations of tinning and hot galvanizing. Tinning is carried out at temperatures between 250° and 300° C., and the wire may therefore be considerably
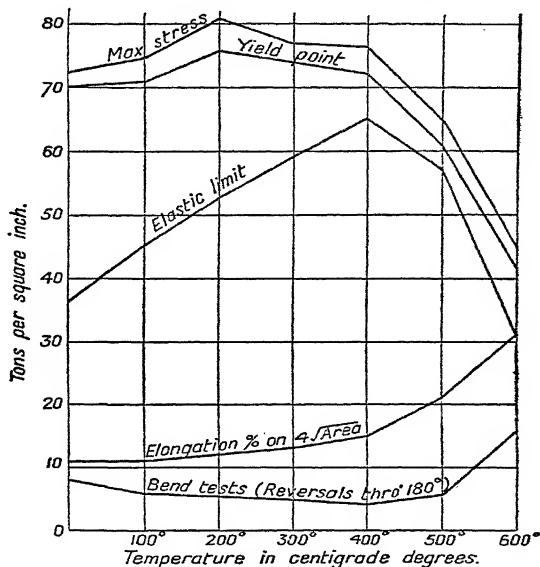
Fig. 146.—Showing the Effects of Tempering on the Properties of Cold-drawn Steel containing 0·45°/₀ C; 0·1°/₀ Si; 0·75°/₀ Mn

embrittled in consequence. Hot galvanizing is effected by passing the wire through molten zinc at a temperature between 450° and 500° C., and if the temperature is too low there is again the possibility of embrittlement, whilst too high a galvanizing temperature may result in a partial annealing with a serious falling off in the tensile strength. Both the above operations are of course intended primarily to increase the resistance to corrosion.

The load-extension diagram for a cold-drawn wire is given in fig. 147, and it will be noticed that the line of proportionality, or elastic line, is only of comparatively short length, and that

there is no marked yield-point. This is typical of cold-worked materials, and also of many alloy steels which have been heat-treated but not cold-worked. In such instances, a *proof stress* is generally demanded, i.e. the stress which produces a permanent deformation of not more than 0·5 (or 0·1 in some instances) per cent of the gauge length. This may be obtained by loading and unloading the test-piece until the desired permanent set results, but is more often obtained from the load-extension curve as follows: A length equivalent to the plastic deformation required is marked off along the extension axis, and a line is then drawn through this point parallel to the line of proportionality; the point where this line cuts the load-extension curve gives the required proof stress.

From fig. 146 it is obvious that tempering increases the elasticity of cold-drawn steel, and that after tempering the load - extension curve becomes like that of an annealed or normalized carbon steel. Temper-
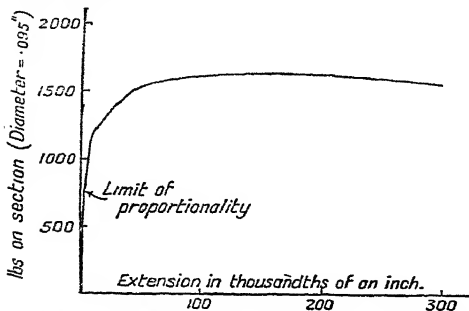
Fig. 147.—Load Extension Curve for Rope-wire cold-drawn to yield 100 tons per sq. in.—readings taken on 4" gauge length.

ing at about 400° C. may yield a value for the elastic limit up to 75 to 80 per cent of the ultimate tensile strength. For this reason, for materials subjected chiefly to tensional stresses, several specifications demand that the steel shall be supplied in the cold-drawn and " blued " condition, which thus necessitates tempering between 350° and 450° C., a treatment which increases the brittle-ness and diminishes the resistance to shock. Thus for such purposes as streamline wires, which are subject to considerable vibration and shock, the original cold-drawn wire is much more satisfactory than a wire which has been blued. Again, blueing has an adverse effect on the torsion values, and is therefore not advisable for parts which are subject to torsional stresses. In view of the increased elasticity obtained by tempering, springs which are made from cold-drawn steels are generally blued before being placed into service, a procedure which experience has shown to be beneficial.

Effects of Annealing on the Properties of Cold-drawn Steels.

Fig. 148 shows the effects of annealing on the properties of a fairly high carbon steel, from which the following conclusions may be drawn:
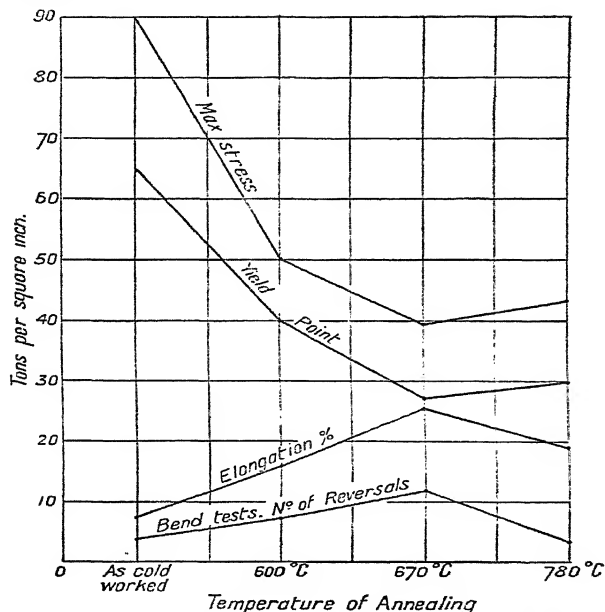
Fig. 148.—Showing Effects of Annealing on the Properties of Cold-drawn Steel

(1) Annealing at temperatures up to 600° C. results in a very marked lowering in the values for the yield-point and maximum stress, and an increase in the ductility as measured by the elongation. The reverse bend test results are only slightly affected.

(2) When the annealing temperature is between 600° and 670° C., the yield-point and maximum stress are still further decreased, but not at former rates. The elongation is improved and much better bend test results are obtained.

(3) Annealing at temperatures above 670° C. results in increased strength, but the elongation and bend tests are adversely affected.

(4) Maximum ductility is obtained by annealing at about 670° C. After such treatment the wire may be bent double without the slightest sign of fracture, and is therefore in the best possible condition for shaping to any desired form, such as for springs, &c.

The microstructure of a cold-worked steel annealed at about 670° C. consists of spheroidized cementite in a ferrite matrix, i.e. the structure is completely divorced, and for a high carbon steel is similar to that shown in fig. 116 (facing p. 150). Such structures are capable of withstanding a very considerable amount of deformation by cold-work, a point to which reference will again be made in connexion with cold-rolling.

In articles not subjected to further heat-treatment, these structures are undesirable in view of the low values of the elastic limit and yield-point. Further, some difficulty may be encountered in obtaining complete solution of the carbide of iron when heating the material for hardening. In such instances, a normalizing treatment at a somewhat higher temperature than that subsequently employed in hardening is advisable.

Defects in Cold-drawn Wire.

As already indicated, many defects in the original hot-rolled rods are readily detected during cold-working, and the process may indeed be regarded as constituting a very severe form of test for the steel. Occasionally, however, it may happen that a wire which is perfectly sound on the surface contains incipient flaws such as those represented in fig. 140. Such flaws are the result of irregular flow during drawing, and may be due to faulty heat-treatment. This defect is readily revealed by means of the alternate bend test, and then verified by the micro-examination of longitudinal sections of the wire. Although a poor bend test result does not necessarily imply internal cuppiness, a wire giving a bad test value should always be sectioned longitudinally and examined under the microscope.

Many failures of wire have been attributed to overdrawing. The cold-drawn condition is a most satisfactory one for many purposes, but Adam * considers that a definite stage is reached beyond which no rope-wire should be drawn. This stage is

indicated by an abrupt change in the tensile strength of the steel, as indicated by the results of tensile tests taken at various stages of the drawing operation.

Unfortunately, there is no simple test to determine whether the steel has been overdrawn, and in many cases little indication is given by the microstructure, although in some overdrawn high tensile wires the usual structure is replaced by one in which the fibres are less clearly marked and this structure more confused. A very convenient test advocated by the late Dr. McWilliam, which serves to indicate a very pronounced degree of overdrawing, consists in immersing the wire for a short time in boiling water. If the wire has been definitely overdrawn, the torsion figures show a very pronounced drop, even though the original cold-drawn material may have given extremely satisfactory values.

For many purposes, such as, for instance, highly stressed springs, a lightly drawn higher carbon steel is considered to yield better results than a more severely drawn lower carbon steel. This is readily understandable since the higher carbon steels are more homogeneous in structure, particularly after patenting, and the flow during drawing is therefore much more uniform. On the other hand, for rope-wire where the carbon content is necessarily fairly high, Adam considers that as low a carbon content as possible should be employed, provided that the necessary tensile strength can be obtained without overdrawing.

Cold-rolling.

The raw material for cold-rolled sheet and strip is the hot-rolled strip not generally less than about 12 G in thickness. As with wire or rod for cold-drawing, scale must be removed by pickling before the steel is cold-rolled. The pickling of strip before cold-rolling is really of much greater importance than the pickling of wire prior to cold-drawing, since many causes of failure of cold-rolled strip are due to the " rolling-in " of scale not removed in pickling. The surface of the material is then defective, its mechanical properties are adversely affected, and what is perhaps of still greater importance, the material will " pit " badly when subjected to corroding influences. This will occur even in alloys of the stainless iron type, and in view of the fact that particles of foreign matter which are rolled into the surface tend to initiate corrosion, one firm of makers of steel strip actually takes the trouble to wash and filter the air which

enters the cold-rolling shop and thus ensure an atmosphere absolutely free from grit. Fig. 149 (facing p. 196) shows a section of a specimen of mild stainless steel which corroded badly even indoors. The particles of rolled-in scale are clearly shown.

After pickling, very low carbon strip may be rolled immediately, but the higher carbon steels are generally annealed. The annealing is carried out in cast-iron pots filled with cast-iron turnings or drillings, which serve to prevent surface oxidation and the formation of scale on the pickled strip. For the higher carbon steels the temperature of annealing is generally below the critical point, since the production of divorced pearlite is rather desirable. A steel with its carbide in the globular condition will withstand cold-rolling and cold-pressing to a much greater extent than a material consisting of either sorbite or lamellar pearlite.

As in wire-drawing, the necessary reduction in section is not generally obtained in one operation, except where the objects of cold-working are merely to stiffen the material and obtain a good surface. Unlike the case of wire-drawing, the first pass in cold-rolling generally involves the greatest reduction in section, and the reduction at each subsequent pass is gradually decreased in view of the very rapid rate at which maximum hardness is developed. Annealing may be necessary at intermediate stages.

As the amount of cold-work by rolling is increased, the tensile strength increases, and the following formula is useful in determining either the reduction in section necessary to yield a strip of specified strength, or as an indication of the tensile strength after a definite amount of cold-work has been applied:

$$M = S + \tfrac{1}{2}R \left\{ \begin{array}{l} \text{where M is the tensile strength of the rolled strip, S} \\ \text{the tensile strength of the strip prior to cold-working,} \\ \text{and R the percentage reduction in thickness by cold-} \\ \text{work.} \end{array} \right.$$

This relationship is merely empirical, as will be evident from the following data:

Per Cent Reduction.	Calculated Tensile Strength.		Actual Tensile Strength.	
0	30·0 tons per sq. in.		30·0 tons per sq. in.	
25	42·5	,, ,,	43·2	,, ,,
31¼	45·65	,, ,,	45·5	,, ,,
41¼	50·87	,, ,,	47·0	,, ,,
49¼	54·62	,, ,,	50·0	,, ,,
60	61·17	,, ,,	51·8	,, ,,

It will be noticed that the calculated and actual values are in very close agreement up to about 40 per cent reduction in section, and the expression finds considerable application.

One of the most useful and widely employed tests on cold-rolled strip is carried out in the Erichsen machine. This test produces a bulge in the strip by means of a dome-shaped die which is gradually forced on to the metal under the influence of a hand-controlled ram until fracture occurs. The drawing depth
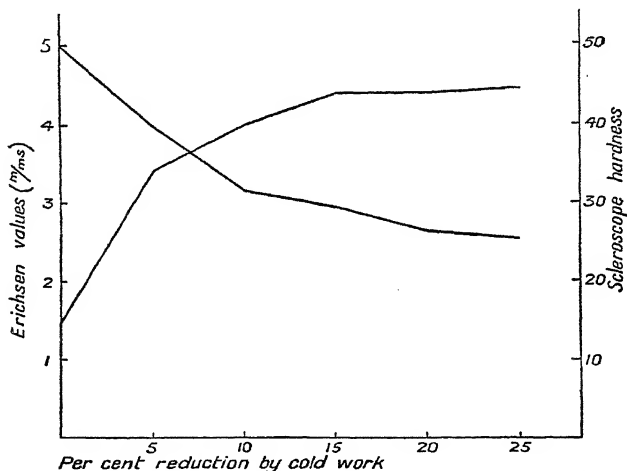
Fig. 150.—Illustrating Effect of Cold-rolling on the Properties of a High-carbon (0·97°/₀) Steel Strip

in millimetres is then read off on the apparatus, and the values thus obtained are of great importance in determining the quality of the metal strip.

The Erichsen values for a high carbon steel strip, each strip tested being of the same thickness, are plotted in fig. 150, and it will be noted that the curve shows a tendency to become asymptotic. Thus, although the Erichsen value decreases rapidly up to about 15 per cent reduction, further cold-work has not nearly so much influence.

Much practical information can be obtained from the examination of the dome produced by the Erichsen machine. If the

fracture runs around the dome, the metal will have a fibrous character and give a low drawing value. Such a steel is not very suitable for withstanding further deformation by bending, folding, &c. A smooth dome indicates a material possessing good drawing properties, whilst a rough surface generally indicates a large coarse-grained material incapable of withstanding much more deformation. Coarse-grained structures render the metal unsuitable for such operations as pressing, and this may be encountered in both ferrous and non-ferrous alloys. This difficulty is caused by over-annealing, i.e. by annealing at too high a temperature.

Summarizing, therefore, a good quality cold-stamping and cold-pressing steel sheet should yield a good Erichsen value and practically no fibrous structure, whilst the dome should be quite smooth and free from surface defects.

In addition to the tensile strength and the Erichsen value, the scleroscope hardness of cold-rolled strip is often demanded in specifications, and from the curve given in fig. 150 it is evident that the scleroscope readings are only very slightly affected beyond 15 per cent reduction by cold-work.

Just as with cold-drawn wires, cold-rolled strips are sometimes hardened and tempered in order to secure a certain desired combination of physical properties. In such instances, the effects of cold-work on the microstructure are almost entirely obliterated, as will be evident from fig. 151 (facing p. 196). Considerable care and skill are necessary in the heat-treatment of thin strip, and some specifications allow a heating period for hardening of not more than two minutes, since a longer period is liable to cause considerable decarburization. In some cases, such as with strip for aeroplane spars, the material under tension is made part of an electric circuit, by which means it is rapidly heated to the desired temperature; and after the current is switched off, a thin strip cools so very rapidly, even in the air, that a true quenching effect is obtained.

Somewhat thicker sections are passed through a continuous furnace and cooled by a blast of air at the exit end.

Considerable care is necessary in preventing excessive decarburization during the several heatings which may be necessary in the production of cold-rolled material, and it may be noted that a lightly rolled strip will yield better results for many purposes than a more severely rolled lower carbon strip. Thus, if decarburization has been excessive, it may become necessary to

cold-work the material more severely than is desired, in order to give the specified scleroscope hardness. Such a material may not prove to be entirely satisfactory in use.

Cold-worked Alloy Steels.

Most cold-worked steels, with the possible exception of the modern high-chromium austenitic alloys, do not contain notable proportions of alloying elements. This is due partly to the fact that the most suitable structure for withstanding cold-work is much more difficult to obtain in alloy than in plain carbon steels. Thus nickel and nickel-chrome steels, in which under ordinary circumstances the effect of the nickel in restraining grain growth during heat-treatment is distinctly advantageous, cannot be readily treated in order to yield the necessary large-grained sorbite suitable for wire-drawing; and frequent annealings, generally between each pass, are necessary both for wire and strip. This materially adds to the cost of production, and there is also the risk of pronounced decarburization. Further, in most cases, the best combination of physical properties for an alloy steel is only obtained after proper heat-treatment. With thin strip, however, uniform thickness is only satisfactorily obtained by cold-rolling, and nickel-chromium steels are used for certain purposes where high tensile strength and great resistance to shock are essential, but the strips are then subjected to a quenching and tempering treatment after being cold-worked. High-speed steels, and the high-carbon steels containing chromium which are employed for ball-bearings, are sometimes cold-drawn into bars and rods. Subsequent annealing then leads to the formation of spheroidized cementite, a structure rather desirable in such materials, since it lessens the tendency towards cracking when the finished articles are hardened.

Stainless steel, which is pearlitic in the slowly cooled state, may be obtained in both the cold-drawn and rolled conditions; but it should be noted that the material is not " stainless " in the cold-worked state, and must be hardened after being cold-worked. The low carbon stainless irons in the cold-worked state offer much greater resistance to corroding influences than does ordinary stainless steel, but in this case also the maximum resistance to corrosion is only obtained after a quenching from about 1000° C. The austenitic nickel-chromium-iron alloys are " non-corrosive " even in the cold-worked state, and are sometimes used in this

condition, although tempering may be necessary to yield other desired properties. The high chromium-nickel non-corrosive steels can be cold-worked to a very remarkable extent, which is not altogether unexpected in view of the facts that they consist of one homogeneous solid solution (austenite), and that the large grain size so desirable in materials which are to be cold-worked is readily induced in them. Fig. 152 (facing p. 196) shows a section of such an alloy in the cold-rolled condition, the distortion of the crystal grains and the abundance of strain lines being clearly marked. In this condition, a proof stress of 55 to 60 tons per square inch may be readily obtained.

Note on the Investigation of Failures

When a material has failed in service, a " post-mortem " examination should always be carried out wherever possible, in order that the cause of failure may be discovered and further trouble avoided. In this connexion the microscope is invaluable, since in many instances it is at once obvious, from the microstructure, that a material has been applied for a purpose for which it was altogether unsuitable. One very glaring example of this kind examined by the author was the failure of several gear wheels reputed to have been made from a direct oil-hardening nickelchrome steel. Microscopical examination of a polished and etched specimen demonstrated very clearly that the material was, in reality, an ordinary plain low carbon case-hardening steel which had been inadvertently mixed with the correct material.

It must be noted, however, that microscopy has its limitations, and in certain cases entirely erroneous conclusions may be drawn from the microstructure if no other information is available. In such instances, extreme caution is necessary against any dogmatic expression of opinion; and as an illustration there may be cited the great similarity which exists between the structure of, say, a quenched and tempered 0·6 per cent carbon steel and an ideally worked and annealed steel containing 1 per cent carbon, in which the carbide exists in a finely spheroidized condition. Again, the apparent carbon content of a steel is greatly influenced by the presence of other elements, and in ordinary steels by the manganese content in particular. The microscope cannot therefore be relied upon to indicate the chemical composition of the

steel, and in any case of failure, a chemical analysis of the material should be carried out wherever possible. The chemical analysis, however, only indicates the average composition, and does not reveal such defects as surface decarburization and non-metallic inclusions. Thus a fairly high silicon content does not necessarily imply a high silicon content in the steel itself, since it may be due to the presence of numerous occluded slag particles containing a large proportion of silica in the form of silicates. It will be evident, therefore, that neither the chemical composition nor the micro-structure alone can always be relied upon in indicating possible causes of failure, but when considered together, much valuable information may be obtained, and, in many cases, the other physical properties of the material may be predicted from this information alone, although in a complete investigation these properties should be experimentally determined.

Summarizing, the chemical composition serves to indicate the suitability of the material for any specific purpose, whilst the microscope reveals such defects as decarburization; the segregation and distribution of impurities such as manganese sulphide, occluded slag particles, &c.; microscopic cracks; and in particular, incorrect heat-treatment.

Micro-specimens should always be cut at right angles to a fractured surface, since if the actual fracture is prepared and examined, the real cause of failure may be removed during the preparation of the specimen. In addition, specimens should be cut well away from the fracture and their structures compared with that near to the actual fractured surface. Articles of comparatively thin section should be examined across the whole cross-section, both at low and high magnifications. For most purposes, magnifications of 50 to 100 and 250 to 500 diameters respectively usually suffice; and, in general, the lower power indicates the structure of the material, whilst the higher powers serve to reveal its constituents.

In many cases, such as forgings, much information may be obtained from the macro-examination of the longitudinal sections. After the surface has been prepared and polished, sulphur prints may be obtained, then the same surface may be etched by one of the copper reagents in order to reveal the macrostructure. As already indicated, sulphur prints serve as a general index to the distribution of the impurities, sulphur and phosphorus, whilst the macro-etched surface reveals the fibre or grain in the steel.

Several causes of failure have already been indicated in the preceding pages, many of which are exclusively metallurgical. Numerous failures occur, however, for which the engineer is solely responsible. Thus a very heavy cut during machining, particularly when a blunted tool is employed, results in a tearing rather than a true cutting action, and the surface layers may be distorted to a very pronounced degree. The surface material is then truly cold-worked, and its impact resistance may be seriously lowered, as will be evident from the data on p. 195. Such material, when placed into service without subsequent heat-treatment, may fail under shock.

The tearing of the surface during rough machining may also give rise to the formation of cracks, and of such depths that they are not removed during the final machining operation. Fatigue cracks then develop in such articles as crankshafts, axles, &c., which are under the influence of dynamic stresses. Machining cracks at the bases of the teeth of milling cutters, large taps, &c., may develop into fractures during hardening.

That the distribution of the stress is not uniform, under load, in a material which is not of uniform section, is generally appreciated by the engineer, but it is not always realized that the stress concentration, due to sudden changes in section, may become so intense and localized that failure readily occurs due to this cause alone. Sharp corners and angles in highly stressed material often lead to failure in service. Further, such defects in the design of the higher carbon steel tools, which are subjected to a drastic hardening treatment, do so almost invariably.

Non-ferrous Engineering Alloys

The non-ferrous alloys are those containing metals other than iron as the chief constituent. In many non-ferrous alloys iron may be almost completely absent; in others, it is to be regarded as an impurity unavoidably present, whilst in some cases the element may be intentionally added, and then becomes an essential constituent.

The most important engineering non-ferrous alloys are those containing large proportions of either copper or aluminium. Thus the copper-zinc alloys or brasses, the copper-tin alloys or bronzes, and the copper-aluminium alloys rich in copper, known as the aluminium-bronzes, are extensively employed for general engineering purposes, whilst the light aluminium alloys of the duralumin type are of particular importance in airship and aeroplane construction.

Copper and its Alloys.

Although pure copper is found native in some parts of the world, most of the copper of commerce is extracted from its ores, notably those containing cuprous sulphide. These are rarely pure, but are generally associated with other elements, notably iron in the form of copper pyrites, $Fe_2S_3 \cdot Cu_2S$. The extraction process is very complex, and depends, in the first place, on the fact that copper possesses a greater affinity for sulphur and a lesser affinity for oxygen than the other elements with which it is associated. When the sulphide ore is roasted, part of the sulphur is oxidized and evolved as sulphur dioxide, together with the gases formed by the oxidation of other impurities originally present in the ore. Some copper and most of the iron is converted into oxides, and when a fusion temperature is reached the oxidized iron combines with silica, either contained in the ore or intentionally added, to yield a slag covering consisting

essentially of ferrous silicate in which other oxidized impurities are dissolved. This slag is then removed from the surface of the liquid, and by repetition of the roasting and fusion practically the whole of the iron may be removed. At this stage the copper exists chiefly as the sulphide, although some cuprous oxide is formed during roasting and fusion. The material is then remelted under conditions which are decidedly more oxidizing than hitherto, in order to bring about further oxidation of the copper. When the oxidation has proceeded far enough the temperature is raised, and metallic copper is then obtained as a result of the reaction:

$$2Cu_2O + Cu_2S = 6Cu + SO_2.$$
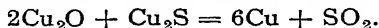
By this means the remaining sulphur is eliminated as sulphur dioxide. Some of this gas, however, is dissolved in the molten copper from which it is liberated during subsequent solidification, with the consequence that the crude metal is honeycombed with blow-holes or " blisters ".

Finally, the " blister " copper is remelted under strongly oxidizing conditions; impurities such as arsenic, antimony, iron, &c., still remaining, being oxidized and skimmed off as a slag. Anthracite coal is then sprinkled on the surface of the molten metal, which is agitated by stirring with wooden poles or " green " saplings. This promotes reduction of cuprous oxide and the flotation of occluded slag particles. Poling is an important operation. If the metal is underpoled, it is too rich in cuprous oxide, is very brittle in consequence, and breaks with a dull-red fracture. On the other hand, overpoling results in the reduction of other impurities from any slag remaining, and in addition, the copper does not contain sufficient oxygen to ensure that the impurities exist as oxides, which exert a much less harmful influence on the properties of the copper than the elements themselves. In the absence of sufficient oxygen, the reduced impurities form weak intercrystalline constituents around the crystals of copper, and the metal, which breaks with a yellowish fracture, is extremely brittle. Correctly poled copper is known as " tough pitch ", and is extremely tough and malleable. When fractured it exhibits a salmon-red colour.

Several other processes for the extraction of copper are carried out. One method which is extensively employed consists in a preliminary treatment of the concentrated ore in a blast-furnace in order to oxidize the iron, which then enters the slag. The

copper, essentially as sulphide, is then, after remelting, run into a Bessemer converter. The air blown in burns out the sulphur, although in this case, also, the solid copper finally obtained is in a spongy form owing to the liberation of dissolved sulphur dioxide during solidification.

Large quantities of copper are also obtained by electrolytic deposition from solutions of its salts. The metal is thus obtained in a high degree of purity, but in this condition is of no engineering value, and is therefore remelted and cast into ingots. During melting oxidation occurs, with the consequence that the metal contains small proportions of cuprous oxide even when melted under a charcoal covering.

Commercial copper is usually obtained in a high degree of purity, but although the proportion of impurities is generally small, these may exert a very harmful effect on its properties. Apart from its use in electrical work, pure copper is much too soft and its tensile strength far too low for most engineering purposes. Enormous quantities are employed in electrical engineering, but the pure metal is unsuitable for castings. This is due to the difficulty in obtaining sound metal free from blow-holes, due chiefly to sulphur dioxide which is readily absorbed from the sulphurous gases formed from the fuel employed in the melting furnace. Unsoundness due to abnormal amounts of copper oxide may be circumvented by the addition of some deoxidant such as phosphorus in the form of phosphor-copper, or manganese, aluminium, zinc, &c., but in many instances the presence of even very small proportions of either of these elements exerts a detrimental influence on the properties of the copper.

As might be expected from the fact that it is a soft, malleable metal, copper may be cold-worked to a very pronounced degree, and the uses to which the cold-drawn bars, tubes, wire, and cold-rolled sheets are put are multitudinous. The various impurities which may be present in commercial copper have a considerable influence on its cold-working properties. This influence is considered in subsequent paragraphs.

The Properties of Copper—Effect of Impurities.

Commercially pure copper may contain as much as 99·9 per cent of the element, and for electrical purposes the impurities may amount to less than 0·05 per cent. When cold-worked and subsequently annealed, the tensile strength is generally about

14 tons per square inch, and the elongation about 30 per cent. For sheets, a bend test is usually applied, and the metal, after being bent through 180°, is hammered, when no cracking should be apparent. Cold-drawn copper may possess a tensile strength of any value between 20 and 32 tons per square inch, but the elongation is then less than 5 per cent.

In the annealed state, the specific resistance of copper is about 1·59 microhms per cm.³, and its temperature coefficient of resistance less than 0·0006 per 1° C. Copper is indeed, with the exception of silver, the best conductor of electricity (and heat) known. In addition to increasing the tensile strength of copper, cold-working increases its electrical resistance and thus decreases its conductivity. The full electrical properties may, however, be completely restored by annealing at a temperature of about 500° C. Annealing at temperatures much higher than this results in abnormal grain growth, and although its electrical properties may be quite satisfactory, the tensile strength of the copper may be very seriously lowered by such treatment.

The condition of the material is readily determined from the microstructure. Thus, if it has been cold-worked to any great extent, the crystals are very much distorted and perhaps show confused masses of strain lines, whilst annealing after cold-working yields innumerable twinned crystals.

In addition to iron, sulphur, and oxygen, commercial copper may contain small amounts of arsenic, antimony, or bismuth. Some of these elements enter into solid solution with the copper, and thus increase its tensile strength, but in most cases the increase in strength is at the expense of its ductility or malleability. Other elements may lower both the strength and the ductility, whilst in almost every instance the electrical properties are adversely affected, a matter which is obviously of great importance in cable work.

Effect of Cuprous Oxide.

Oxygen exists in copper in the form of cuprous oxide, Cu_2O, which is soluble in liquid copper but only very slightly soluble in the solid metal, and cuprous oxide and copper may be considered as yielding a very simple binary system of the type given in fig. 48 (p. 73), the eutectic being obtained at about 3·5 per cent Cu_2O (or 0·39 per cent of oxygen). This amount of oxygen is readily absorbed by melting the copper in air without any protective

coating. The melting-point of pure copper is 1083° C., and that of the eutectic 1064° C. The ease with which the eutectic is obtained by atmospheric oxidation alone has led to its application as a standard for the calibration of pyrometers, and it is often preferred to pure copper, since in the latter case elaborate precautions against oxidation become necessary if a sharp melting-point is to be recorded.

When the metal is slowly cooled, the cuprous oxide in the eutectic becomes spheroidized, the globules being readily identified by their sky-blue colour when unetched specimens are examined under a microscope employing a " dry " objective.

A small proportion of cuprous oxide is considered to be essential in copper which is to be cold-worked, but if it is present in greater quantity than 0·1 per cent, the eutectic may exist as a complete network around the crystals of pure copper. This embrittles the material, which tends to crack when worked, either hot or cold, and also when subjected to the action of reducing gases such as hydrogen. The latter operation is known as " gassing ", the formation of intercrystalline cracks being due to the penetration of hydrogen along the crystal boundaries. Steam under considerable pressure is thus produced, which forces the copper crystals apart. Copper containing much oxide should therefore be annealed in an oxidizing atmosphere.

Effect of Arsenic.

Arsenic increases the tensile strength of copper but lowers its elongation, although the latter is not seriously affected up to 2 per cent arsenic, as will be observed from the following data, due to Bengough and Hill: *

Arsenic, per cent.	Oxygen, per cent.	Y.P., tons/sq. in.	M.S., tons sq. in.	Elongation, per cent.	Reduction of Area, per cent.
0·04	—	6·25	15·50	58	78
0·25	0·12	9·50	15·75	50	
0·75	—	6·20	15·65	57	
0·94	0·15	8·65	16·55	55	70
1·91	0·20	6·55	16·90	52	80

In such amounts, most of the arsenic exists in solid solution in the copper, but if the metal contains oxygen copper arsenite is formed. This is insoluble in the copper, existing as isolated globules within the copper crystals, and has a disposition in the microstructure

similar to that of slag in wrought iron. Arsenic thus tends to counteract the embrittling tendency of abnormal amounts of oxygen, and the tendency to develop cracks when the material is subjected to the action of reducing gases is much less marked. Although " arsenical copper " is not altogether immune from the effects of gassing, particularly at high temperatures, the effects are much less pronounced than in copper containing oxygen but free from arsenic.

The effects of annealing on the structure of cold-worked arsenical copper are shown in fig. 153 (*a*) and (*b*), whilst (*c*) shows the extent to which grain growth may occur after the material has been gassed at a very high temperature.

Arsenical copper is employed for locomotive fire-boxes, boiler tubes, stay bolts, and rivets, the arsenic contents generally varying between 0·25 and 0·5 per cent. The material is generally used in the cold-worked state; and the following tests, due to Hughes,* may be accepted as typical of the material in this condition:

Compositions of Three Different Samples.	Average Tensile Test Values.
1. Copper, 99·3%; arsenic, 0·46%	Maximum stress, 14·66 tons/sq. in.;
2. ,, 99·32%; ,, 0·43%	Elongation, 43·4 per cent; Re-
3. ,, 99·3%; ,, 0·51%	duction of area, 44·9 per cent.

Effects of other Impurities.

Iron may be found in commercial copper. The proportion of this element should be kept as low as possible since it forms solid solutions which are rather brittle.

Small amounts of *antimony* injure the cold-working properties of copper, and also decrease its electrical conductivity. If sufficient oxygen is present, however, copper antimonite is formed, and the properties of the copper are then affected to a much smaller extent.

As already indicated, *phosphorus* is sometimes employed as a deoxidant in castings. For electrical work an excess of phosphorus must be avoided, as will be evident from the fact that only 0·075 per cent phosphorus is required to lower the electrical conductivity to about one-half that of pure copper.

Sulphur, as cuprous sulphide (Cu_2S), lowers the ductility and affects the malleability of copper. If much sulphur is present the copper may be very brittle, and for this reason many specifications limit the sulphur to 0·01 per cent.

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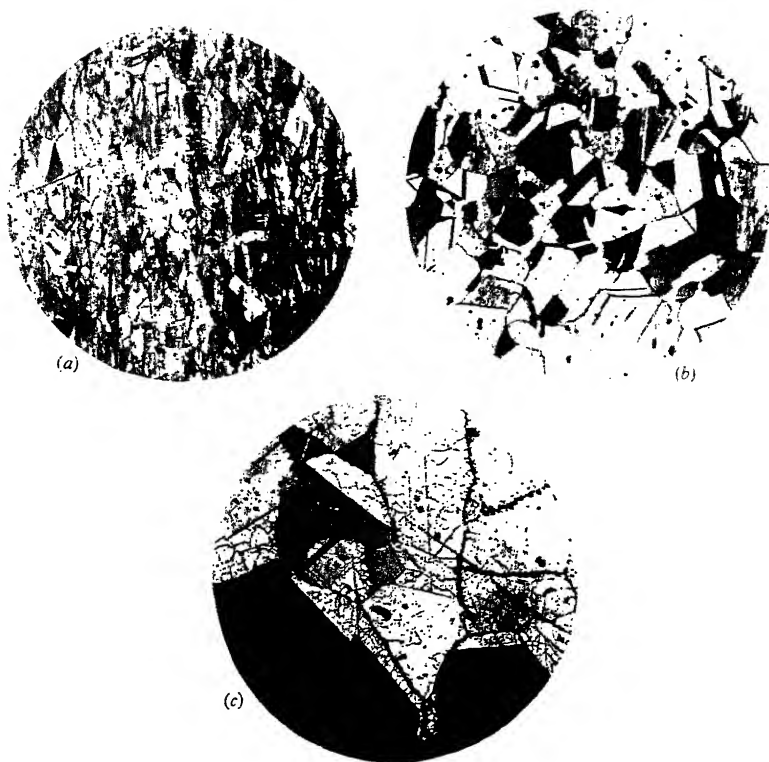
Fig. 153.—Arsenical copper: As, 0·45 per cent.   (a) Hammered.
(b) Hammered and annealed.   (c) After being " gassed " between
800 and 900° C.   ×75.

Very small amounts of *bismuth* exert a disastrous influence on the properties of copper. This element forms a eutectic with copper which exists in the form of thin films at the boundaries of the copper crystals. The bismuth-copper eutectic is exceedingly brittle, and such a small amount as 0·001 per cent Bi seriously affects the cold-working properties of copper. At higher temperatures the influence of bismuth is even worse. The melting-point of the eutectic is only 268° C. Above this temperature, the crystals of copper are therefore held together by the liquid eutectic, with the consequence that the material disintegrates when the slightest stress is applied.

Tellurium also exerts a harmful influence on the properties of copper. Its effect is similar to that of bismuth, and 0·002 per cent renders the copper very brittle indeed.

Silicon may be present as an impurity in commercial copper, but in some cases small amounts of silicon are intentionally added. If silicon is not present in too great a quantity, the tensile strength of the copper is improved, and its electrical conductivity is not seriously affected. Copper containing up to 0·2 per cent Si is frequently employed for telegraph and telephone wires.

Brasses.

The alloys of copper and zinc are probably the most important non-ferrous engineering alloys. These alloys cover a wide range of physical properties, and their applications are very wide and varied. The part of the copper-zinc equilibrium diagram which is of importance from an engineering standpoint is given in fig. 154, from which it will be observed that copper is capable of holding about 39 per cent of zinc in solid solution at ordinary temperatures, although singularly enough the solubility decreases at higher temperatures, as indicated by the line FG. Up to 39 per cent of zinc, the alloys exhibit similar properties, although the strength gradually increases with increasing proportions of zinc and the colour of the alloys becomes more yellow. Alloys containing less than 39 per cent of zinc are known as the α brasses. These α alloys are always " cored " in the cast condition, but homogeneous crystals may be obtained by annealing (figs. 155 and 156). The annealed α brasses are capable of withstanding a truly remarkable degree of deformation by cold-work without the slightest sign of fracture, a property which renders them particularly suitable for rolling into sheets, drawing into tubes and wire

or rod, and for deep stampings. In the annealed state, the sectional area may be reduced by as much as 90 per cent without any sign of cracking. The capacity for withstanding cold-work is not nearly so pronounced in the cast state, and for tubes, sheets, &c., an α brass should always be annealed before being cold-worked, and particularly when the alloy contains more than 35 per cent of zinc. In α alloys rich in zinc there is always the possibility that the coring may result in the presence of some β solid solution. The β constituent is stronger than the α solid solutions, and thus resists deformation to a much greater degree, with the consequence that cracks readily develop when only a moderate amount of deformation is applied. The β solid solution in such alloys, due solely to coring, disappears completely during annealing.

Fig. 154.—Equilibrium Diagram for Alloys of Copper and Zinc

The addition of zinc to copper results in increased strength, although this is accompanied by a lowering of the ductility. In the α solid solutions, the best combination of tensile strength and ductility is obtained with the alloys containing about 30 per cent of zinc. These alloys, which are often referred to as the "70/30" brasses, are very widely employed for cartridge cases, condenser tubes, &c.

The microstructure of a cold-worked α brass consists of distorted solid solution crystals containing numerous strain lines. Subsequent annealing then results in a recrystallization of the amorphous phase and the development of numerous twinned crystals. The physical properties of the material are then of the

Fig. 155.—70–30 brass in cast state: typical cored structure of α solid solutions. ×15.

Fig. 156.—70–30 brass annealed. ×15

Fig. 157.—"Burnt" brass, showing oxide "spots" and evidence of incipient fusion. ×20.
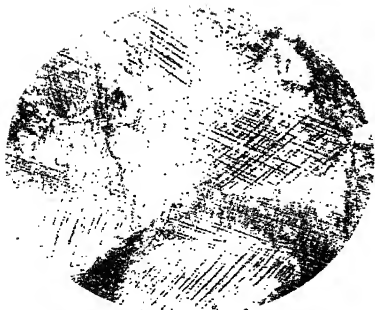
Fig. 158.—70–30 brass which has been annealed and subsequently cold-worked. ×25.

Fig. 159.—70–30 brass cold-worked and then annealed. ×50

same order as those of the original annealed and unworked metal, but both the tensile strength and the ductility are generally higher than in the cast and annealed specimens.

The properties of cold-worked and annealed brass are influenced by the temperatures employed in annealing. For instance, there is apparently a definite minimum temperature somewhat dependent on the degree of cold-work to which the metal has been subjected, below which recrystallization does not occur, and in most cases annealing below 300° C. has very little influence on the physical properties. A cold-worked α brass is not fully annealed, and the maximum ductility is not obtained unless a temperature between 500° and 600° C. is employed. The greater the degree of cold-work the lower is the temperature necessary for full annealing.

When annealed at higher temperatures than the above, grain growth occurs, the twinning may disappear, and the strength of the brass is lowered very considerably. Coarse-grained structures in the finished state are altogether undesirable for most purposes, but are to be preferred if the material is to be subjected to further cold-work.

If still higher annealing temperatures are employed, incipient fusion accompanied by volatilization of some of the zinc may result. The brass is then described as being " burnt ", and is valueless excepting as scrap for remelting, since its ductility is practically nil. The structure of a burnt brass is shown in fig. 157.

High-quality " 70/30 " brass is generally made from very clean scrap and the purest copper and zinc obtainable. Most specifications demand iron less than 0·1 per cent and bismuth less than 0·005 per cent, since these elements have a similar effect on the properties of α brass to that on copper.

Typical microstructures are shown in figs. 158 and 159, and the following tests represent average values:

Condition.	Y.P., tons/sq. in.	M.S., tons/sq. in.	Elongation, per cent.	Brinell No.
Chill cast	5·5–6·0	15·0–16·0	55·0	50–65
Hard-drawn	17·0–22·0	28·0–38·0	5·0	140–200
Hard-drawn and annealed	6·0	19·0–22·0	60·0–65·0	60

Although the α brasses may be cold-worked to a very pronounced degree without detriment, they do not work at all well when hot, and if work is applied at high temperatures the material tends to crack and disintegrate.

α-β and β Brasses.

When the zinc content of a brass is increased beyond 39 per cent, a new solid solution makes its appearance in the slowly cooled or annealed alloys. As the zinc content increases, this β solid solution increases at the expense of the α solid solution until eventually, at 46 per cent zinc, the slowly cooled alloys consist entirely of this β constituent, and homogeneous structures are obtained up to about 49 per cent zinc, when still another new solid solution is formed. The β brasses are thus confined to comparatively narrow limits, but by reference to the diagram given on p. 216 it will be seen that the lines HK–LM, which mark the limits of the existence of the wholly β solid solution, show considerable divergence at higher temperatures.

The γ constituent which appears with a zinc content greater than 49 per cent is very hard, but so extremely brittle that alloys containing it are useless for most engineering purposes. One notable exception is the alloy used for " brazing ". *Brazing brass* contains about 50 per cent of zinc, and is widely employed on account of its comparatively low melting-point. In a good brazed joint, however, the amount of the actual brazing material is kept down to an absolute minimum, with the general consequence that diffusion of zinc into the adjacent parts occurs to such an extent that very little of the brittle γ constituent is found in the join. Brass for brazing should be practically free from lead, since this element tends to penetrate along the crystal boundaries, the metal becoming very weak in consequence. This intercrystalline penetration of lead is most strongly marked in brass which has been cold-worked but not annealed, and thus the danger associated with the use of an ordinary lead-tin solder for cold-worked brass is at once obvious. A brazed joint is therefore always to be preferred to a soldered joint, and a common solder should only be employed for very ordinary purposes where strength and ductility are of little moment.

The β brasses are of importance, since they have found considerable application in marine work in view of their pronounced corrosion-resisting properties. As already indicated, the β region is very narrow, and there is the possibility that the alloys may contain a little too much zinc, and therefore prove unsatisfactory owing to the presence of some of the very brittle γ constituent. In such instances the only remedy is to remelt the alloy with more copper.

With the exception of the α brasses, the copper-zinc alloys containing between 39 and 46 per cent of zinc are of the greatest importance. Such alloys are known as the α-β brasses, and find extensive engineering application.

The β solid solutions have a reddish tint, and the α-β alloys are thus distinctly more red in appearance than most of the α alloys. The effect of increasing additions of zinc on the properties of the annealed alloys is shown in fig. 160, due to Charpy, from which it will be seen that the β solid solutions are stronger but less ductile
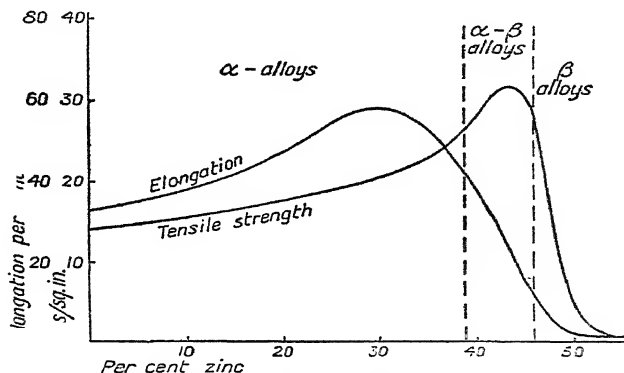
Fig. 160.—Showing Effect of Increasing Proportion of Zinc on the Properties of Annealed Brasses

than the α solutions. In the α-β alloys, the best combination of properties is obtained with about 60 per cent of copper and 40 per cent of zinc. The alloys containing between about 62 and 58 per cent of copper were originally developed by G. F. Muntz, and a "60/40" brass is often known as *Muntz metal*. Alloys of this type have a marked resistance to corrosion, and since they may be readily hot-worked, are extensively employed for hot-stampings, and rolling into sheets and rods for the manufacture of bolts, pins, spindles, &c.

Considerable quantities of Muntz metal are also used for castings for pump parts, &c., and the following data are typical of the material in the cast state:

M.S., tons per sq. in.	Elongation, per cent.	Brinell No.
22·0—25·0	40·0—45·0	89—100

For the larger castings, the zinc content is generally rather higher than for smaller castings. Certain precautions must be taken if satisfactory castings are to be obtained. A high casting temperature results in the formation of long columnar crystals, and the final product may be deficient in strength and lacking in ductility and resistance to shock. As in any other castings, sharp corners and sudden changes in section should be avoided where possible, otherwise there is the risk of the formation of zones in which impurities have been entrapped between the columnar crystals developed from adjacent mould faces. Care must also be taken to minimize blow-hole formation. The metal is generally melted under a charcoal covering, but since this does not always suffice to yield perfectly sound castings, small amounts of some deoxidant are sometimes added.

Casting strains are readily developed in brass, and a considerable amount of distortion may occur during subsequent machining, for which a preceding annealing is the only remedy.

By reference to the copper-zinc diagram on p. 216, the microstructure of a cast 60/40 brass will be readily understood. Thus the alloy commences to freeze at about 900° C. β solid solution crystals are deposited, and the material is completely solid below about 875° C., at which temperature the structure consists entirely of β crystals (which may be " cored "). This structure persists until a temperature of about 725° C. is reached, but below this temperature the β solid solution progressively deposits its α conjugates, at first along the crystal boundaries, and subsequently along the cleavage planes of the pre-existing β crystals. This deposition is progressive down to about 500° C., below which little or no alteration in structure is apparent. The resulting microstructure is of a distinctly Widmanstätten type (fig. 161), although a combination of this structure and a cellular pattern is often observed.

Annealing of α-β Brass.

The changes in structure detailed above occur in the reverse order when the cast metal is reheated, and the structure and properties of cast Muntz metal may thus be modified very considerably by the process of annealing. On reheating to temperatures above 725° C., the whole of the α solid solution is redissolved, and the structure then consists of homogeneous β crystals. If the temperature employed in annealing is not much above the line HK,

Fig. 161.—60–40 brass in cast state. α, light; β, dark. × 50

Fig. 162. — 60–40 brass after being hot-worked: islands of α in β matrix. · 50.

Fig. 163.—60–40 brass quenched from the upper part of the α-β region. Showing " spines " of α in and along the boundaries of the β crystals. Note the comparatively large sizes of the β crystal grains. × 50.

the grain size will be very small, and when the alloy is cooled at a moderately slow rate the resulting microstructure resembles that of an annealed medium carbon steel, rounded masses of the α solid solution being laid over the background of the β constituent. Although such treatment may result in a lowering of the tensile strength, the ductility is improved, and casting strains are entirely eliminated.

The temperature of annealing is of extreme importance. After the α phase has been completely dissolved, grain growth occurs in the resulting homogeneous β crystals at an extraordinarily rapid rate, and if the material has been drastically overheated slow cooling yields a coarse angular structure. Both the strength and the ductility are then adversely affected, and on this account Stead and Stedman * consider it undesirable to anneal the α-β brasses between 750° and 800° C.

The industrial alloys frequently contain small proportions of impurities, and these have their effect on the copper-zinc system. For this reason, the temperature employed in annealing is generally between 600° and 650° C. If much lower temperatures are employed, most of the α remains undissolved, and the tendency is to reproduce the cast structure. The α-β brasses may be cold-worked, but to a limited extent only. After being heated to a temperature within the homogeneous β range, however, the alloys may be hot-worked or extruded without difficulty.

In hot-working or extrusion, the best results are obtained if the work is completed during the time that the α solid solution is being deposited. In the case of rolled materials, this yields a fibrous type of structure, which Desch has shown to be generally associated with good machining properties. If worked at too low a temperature, however, the brass in reality becomes cold-worked, even though its temperature may exceed 500° C., and may crack if severely worked at such temperatures.

After hot-working and annealing, a 60/40 brass exhibits the structure shown in fig. 162, and may then yield the following test results:

Y.P.	M.S.	Elongation, per cent.	Brinell No.
11·5	25·0	40·0–50·0	96–100

If an α-β brass is heated to a temperature within the wholly β region and quenched in water, the tendency is to prevent the

deposition of the α phase which occurs with normal but slower rates of cooling, and thus to retain the structure existing at the moment of quenching. Actually, however, the whole of the α phase is not completely retained, but some of it is deposited during quenching, and then exists as " thorns " or " spines " along the boundaries of the β crystals (fig. 163, facing p. 220). Quenching a 60/40 brass decreases its ductility whilst increasing its tensile strength, and it is worthy of note that the strength of the quenched alloy is retained to a much greater degree at elevated temperatures than is that of the previously unquenched material raised to the same temperatures.

Season Cracking.

Many copper alloys—including the α and the α-β brasses—are liable to season cracking, i.e. the development of cracks after the finished articles have been in service for some time. This effect, which occurs quite spontaneously, is due to internal stress, the sudden release of which results in the production of intercrystalline cracks. The trouble is almost entirely overcome by tempering the material between 280° and 300° C., a treatment which does not materially affect its structure or its properties.

A useful test which serves to indicate whether the material is liable to develop season cracks consists in immersing it for a short time in dilute nitric acid and then in a 1 per cent solution of mercurous nitrate containing a little nitric acid. If the material is in a state of internal stress and therefore liable to season cracking, cracks are developed within a period of about 30 seconds. Fig. 164 (facing p. 226) shows the cracks developed by the foregoing treatment in a specimen of heavily cold-worked " 70/30 " brass.

Effects of other Elements on the Properties of the Brasses.

Lead is sometimes present in brass, either as an impurity or as an intentional constituent. The element is insoluble in copper and its alloys, both in the solid and liquid states, and is readily observed in the microsections in the form of globules when the unetched specimens are examined. Lead exerts a very harmful effect on the cold-working properties of the α brasses, and also lowers both their tensile strengths and ductilities. Good quality brass for either cold- or hot-working should not contain more than 0·1 per cent of lead.

Brasses of the 60/40 type are often employed for castings to be used as containers where no great strength is required, and where

easy machining and a good finished surface are the chief considerations. In such instances, the addition of lead up to a maximum of about 2 per cent is of benefit where easy and rapid machining is desired. For such purposes it is essential that the particles of lead be evenly distributed. This is only satisfactorily secured by carefully controlling the casting temperature, stirring before casting, and by the quick chilling of the metal after it has entered the mould. The following tests were obtained on a brass containing 59·2 per cent copper, 39 per cent of zinc, and 1·7 per cent lead:

Y.P.	M.S.	Elongation.
7·5	18·0	18·0

The tensile strength may be improved by the introduction of tin and manganese, the alloy still retaining the good machining properties due to the lead. Thus a brass of the composition: copper, 58·4 per cent; zinc, 39·1 per cent; lead, 1·6 per cent; tin, 0·4 per cent; and manganese, 0·4 per cent, gave the following results:

Y.P.	M.S.	Elongation.
18·4	26·2	19·1

Tin is only very slightly soluble in α brasses, and although the solubility is apparently increased by rolling and annealing, an excess of the element in such alloys may yield a hard brittle constituent which greatly impairs their cold-working properties. Tin is a constituent of *Admiralty brass*. This alloy is essentially a 70/30 brass to which tin has been added to increase its resistance to corrosion. In view of the great difficulty in obtaining complete solution of the hard tin-rich constituent in the solid state, more than 1 per cent tin is inadvisable. Admiralty brass thus has the approximate composition: copper, 70 per cent; zinc, 29 per cent; tin, 1 per cent. The alloy is cold-drawn into tubes, and also rolled into sheets for condenser plates, but it is necessary to anneal it before cold-work is applied. In the cold-worked state the material may yield a tensile strength of about 40 tons per square inch, with an elongation up to 10 per cent. Tin is more soluble in the β phase and, so it is claimed, increases its resistance to corrosion by sea-water. Large quantities of castings are made from an alloy known as *naval brass*, so called from its wide application in marine engineering. Naval brass may be regarded as Muntz metal to which tin has been added, the composition varying between the following limits: copper, 62–60 per cent; zinc, 39–37 per cent; and tin,

1–1·5 per cent. The following tests are typical of the material in the annealed state:

	M.S.	Elongation.
	26·0	30·0–35·0

Naval brass may be hot-worked, and is employed for bolts, spindles, &c., for purposes where resistance to corrosion by sea-water is essential. Johnson * advises a thorough annealing of the material, followed by slow cooling, before mechanical work is applied.

Certain elements when added to brass enter into solid solution and exert a similar effect on its properties as increased zinc additions, but to a greater or lesser degree. Guillet has assigned to these elements what is described as a " fictitious zinc content ". Thus:

1 part of silicon is equivalent to 10 parts of zinc
1   ,,   aluminium   ,,   ,,   6   ,,   ,,
1   ,,   tin   ,,   ,,   2   ,,   ,,
1   ,,   lead   ,,   ,,   1   ,,   ,,
1   ,,   iron   ,,   ,,   0·9 ,,   ,,
1   ,,   nickel   ,,   ,,   0·8 ,,   ,,
1   ,,   manganese   ,,   ,,   0·5 ,,   ,,

Thus, if these elements are not present in too great a proportion, a brass of rather complex composition may often be referred to a pure brass as regards its microstructure and mechanical properties. The constituents are not identical of course, and the mechanical properties of the brass will vary to some extent accordingly. The relationships given by Guillet are of value, however, as the following examples show:

(*a*) A brass containing 37·5 per cent of zinc and 1·5 per cent of tin would have a zinc equivalent of $37·5 + 3 = 40·5$ per cent, and this brings the alloy well within the α-β region, although from the actual zinc content, and by reference to the diagram, an α brass might be inferred.

(*b*) At first sight, an alloy containing 58 per cent copper, 39·5 per cent zinc, and 2·5 per cent aluminium would be expected to yield a typical α-β brass. In reality, its zinc equivalent would be about $39·5 + 15 = 54·5$ per cent, and the alloy would thus contain the γ solid solution, and be very brittle in consequence.

Certain elements appear to exert a more powerful influence on the properties of brass than a corresponding increase in the zinc content. Thus, if not present in too great a quantity, man-

ganese, nickel, iron, and aluminium increase the tensile strength of brass without seriously affecting its ductility. Alloys containing one or more of these elements, in addition to copper and zinc, are widely employed under the name of " high tensile brass ". Well-known alloys of this type are *Delta metal* and the so-called *Manganese bronze.*

The term " Delta metal " was originally applied by its inventor, A. Dick, whose original patent provided for the addition of 2 or 3 per cent of iron to a comparatively pure brass of the α-β type. Now, however, Delta metal may contain as much as 1 per cent of manganese, and smaller proportions of other elements in addition to iron.

Iron is soluble in both the α and β phases of brass, but to a limited extent only. Even small additions of iron exert a very marked " refining " influence on the usual Widmanstätten structure of a cast α-β brass, as will be evident from fig. 165, an influence which persists in the hot-worked material and improves the mechanical properties of the alloy. Too much iron results in the formation of an iron-rich solid solution, which is intensely hard and gives rise to great difficulty in the machining of castings containing it. This constituent is particularly liable to segregation, and it is therefore very important that the iron content of a brass should be carefully controlled. The most satisfactory tests are obtained with an iron content not greater than 2 per cent. In such proportions each 1 per cent of iron raises the tensile strength of a hot-worked 60/40 brass by about 3 tons per square inch.

Delta metal is a truly remarkable alloy: when heated to above 550° C., it may be forged, rolled, stamped, or pressed into almost any required shape or form. Extruded bars are made in large quantities, and the alloy is frequently employed for castings, which may be either chill or sand-cast. In the cast state the tensile strength is about 20 tons per square inch only, with an elongation of 5–6 per cent, but after hot-working a strength of about 32 tons per square inch is obtained, the elongation rising to 20–25 per cent. The alloy possesses very pronounced corrosion-resisting properties, and is often employed as a substitute for mild steel in castings of intricate shape where resistance to corrosion is also a primary consideration.

Manganese is often added in quantities up to 2 per cent to the 60/40 copper-zinc alloys. Such alloys are known as the " manganese bronzes ", but the term is misleading since tin is not an

essential constituent, and the alloys are brasses in the generally accepted sense.

Manganese is a powerful deoxidant; even a very small proportion of the element (say 0·02 per cent) improves the mechanical properties of a 60/40 brass to which it is added, and leads to the production of sounder castings.

The true manganese bronzes contain about 1 per cent of manganese, and since this metal is generally introduced in the form of ferro-manganese (80 per cent), the alloys also contain some iron. Smaller proportions of tin, lead, or aluminium may also be present, but the alloys are essentially α-β brasses in that they yield Widmanstätten structures in the cast state, and must be worked hot. The manganese (and iron) enters into solid solution and increases the strength of the brass, and even in the cast state a tensile strength of 28–33 tons per square inch may be obtained with an elongation of 30–40 per cent.

Manganese bronze exhibits a pronounced resistance to attack by sea-water, and is therefore often employed for propellers, rudders, and ships' fittings. Sir H. Fowler,[*] in a very interesting lecture on the use of non-ferrous metals in engineering, mentions the use of this alloy for railway axle boxes. These are liable to be hammered in service, and although the alloy resists breaking from this cause, the same authority considers the material too soft to withstand abrasion.

Of the other elements which are intentionally added to brass, *aluminium* and *nickel* are the most important. From the list of equivalents given on p. 224 it is evident that aluminium may replace a large proportion of zinc, and if the aluminium content of a brass is greater than 4 per cent the material is lacking in ductility, and cannot be worked either hot or cold owing to the presence of some of the brittle γ solid solution. Small proportions of aluminium increase the tensile strength of brass, the ductility remaining practically unaffected.

Nickel has a coefficient of equivalence less than unity, and its effect is therefore to increase the apparent copper content of the brass. The element may thus improve both the strength and the ductility. A brass containing 3–4 per cent of nickel, 40 per cent of zinc, and 56–57 per cent of copper in the annealed state may be expected to yield a tensile strength of about 30 tons per square inch with an elongation of 35–40 per cent.

[*] *J. Inst. Met.*, **1924** (i).
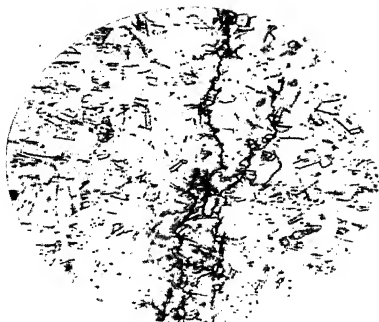
Fig. 164.—Showing season cracks in heavily cold-worked 70–30 brass. × 35.

Fig. 165.—60–40 brass containing 0·03 per cent of iron. In cast state and rather quickly chilled. × 50.
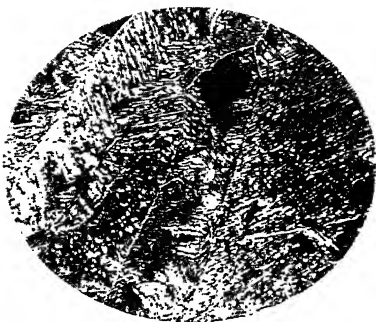
Fig. 167.—Bronze containing 8 per cent of tin in the cast state, cored α solid solution with α-δ eutectoid as infilling. × 100.

Fig. 168.—Annealed bronze containing 8 per cent of tin, homogeneous α solid solution crystals and minute holes resulting from the absorption of the α-δ eutectoid. × 100.
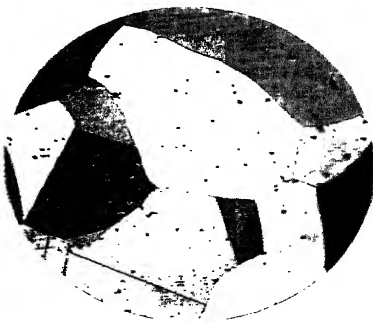
The industrial brasses are rarely pure, and, in addition to the elements already mentioned, may contain small proportions of phosphorus, arsenic, antimony, and bismuth. *Phosphorus*, if below 0·05 per cent, does little harm, and although less than 0·35 per cent of *arsenic* is not particularly injurious, the element is generally kept as low as possible in high-quality brass. Both *antimony* and *bismuth* yield brittle intercrystalline films in α and α-β brasses, and in a good brass either element is usually limited to 0·01 per cent.

It is thus evident that in a complex industrial brass the effect of each element in its relation to the microstructure and the mechanical properties requires careful consideration.

The Bronzes.

That part of the copper-tin diagram which is industrially important is given in fig. 166. Under perfect equilibrium conditions a series of α solid solutions are obtained with less than 14 per cent of tin, although the solubility of tin in the α phase is less at temperatures above 510° C. than at lower temperatures. At 790° C. the limiting α solid solution contains 10 per cent of tin only.

A peritectic change occurs at 790° C. in the alloys containing between 10 and 25 per cent of tin, giving rise to the formation of a β solid solution containing 21 per cent of tin. The tin concentration of this β phase increases as the temperature falls, until at 510° C. it is about 27 per cent. At this temperature the β constituent breaks down into a eutectoid consisting of α and δ solid solutions containing 14 and 32 per cent of tin respectively.

Fig. 166.—Equilibrium Diagram for Copper-tin Alloys (bronzes)

The β solid solutions are only stable, therefore, at temperatures above 510° C , and alloys con-

taining between 14 and 32 per cent of tin are usually known as the α-δ bronzes.

With more than 32 per cent tin the intermetallic compound, Cu_3Sn, makes its appearance. This compound, and the solid solutions containing it, are exceedingly brittle, and the alloys are then of no engineering value.

α Bronzes.

Alloys containing up to 6 per cent of tin exhibit similar properties to the α brasses, although the bronzes are stronger than the corresponding copper-zinc alloys. Thus the α bronzes are heavily cored in the cast state, but equilibrium may be restored, and homogeneous solid solutions obtained, by annealing. After annealing, the alloys can be cold-worked, and strain lines readily develop, whilst annealing after cold-working results in the formation of numerous twinned crystals just as with the α brasses.

Bronzes should be melted as rapidly as possible, otherwise undue oxidation of some of the tin occurs, with the result that numerous particles of oxide are occluded in the solid alloys. Tin oxide " spots " are readily identified under the microscope by their blue colour, and are generally surrounded by halos as a result of the action of the etching medium. Much oxide of tin lowers the ductility of bronze, and may seriously affect the cold-working properties of the α alloys although they may have been thoroughly annealed. For this reason the bronzes frequently contain small proportions of phosphorus added as a deoxidant in the form of phosphor-copper, and although the final product may contain mere traces of phosphorus, both the strength and the ductility are improved as a consequence of the more thorough deoxidation. Too much phosphorus, however, leads to the formation of a hard brittle constituent rich in phosphorus, and the alloys containing it are unsuitable for cold-drawing or cold-rolling.

Alloys containing more than 6 per cent of tin cannot be cold-worked satisfactorily; the alloys are so very heavily cored in the cast state, and then contain so much of the α-δ eutectoid, that there is the greatest difficulty in obtaining homogeneous solid solutions even with a very prolonged annealing.

The addition of tin to copper results in increased strength. A maximum is obtained with between 9 and 10 per cent of tin, however, and the ductility falls rapidly with a higher tin content. In the cast and slowly cooled state a bronze containing about 10

per cent of tin will give a strength of between 14 and 16 tons per square inch, with an elongation of about 15 to 18 per cent.

Bronzes containing this amount of tin find many engineering applications where considerable strength is required, e.g. for bearings, pumps, gears, nuts, &c. Theoretically, after being slowly cooled, such alloys should consist entirely of the α solid solutions. In the cast state, however, these bronzes always show some of the α-δ eutectoid even when very slowly cooled. All the α bronzes are very heavily cored in the cast condition, and, as a consequence, a 10 per cent tin alloy does not become completely solid immediately 790° C. is reached; the average composition of the already deposited α solid solution is somewhat less than 10 per cent tin, and some liquid still remains. This liquid then reacts with some of the solid already deposited to yield the β solid solution containing 21 per cent of tin, which eventually breaks down into the eutectoid at 510° C. Since this eutectoid is formed from the liquid which is last to freeze, it is entrapped between the branches of the dendrites. If such a bronze is thoroughly annealed the cored structure disappears, and the α-δ eutectoid is absorbed in the α phase. Annealing may lead, however, to the production of cavities in the alloy, since the homogeneous solid solution produced by the solution of the α-δ eutectoid (or rather, the β solid solution formed at the annealing temperature) is denser than the original.

Annealing considerably improves the ductility of such bronzes, but the alloys may become porous owing to the cavities left in them as a result of the absorption of the α-δ eutectoid. This matter is of obvious importance in connexion with pumps, steam fittings, &c., since the material may allow water, steam, or oil to pass through, and for such purposes an annealing treatment is harmful rather than otherwise. Alloys of this composition for use as bearings should never be annealed, since the α-δ eutectoid which is present in the cast state is essential for resisting wear.

Micrographs of a bronze containing about 8 per cent of tin are shown in figs. 167 and 168 (facing p. 226). A 10 per cent tin bronze exhibits similar structures, although the cast specimen contains more of the α-δ eutectoid, and a very prolonged annealing is necessary to effect its complete absorption.

If a bronze is annealed at a very high temperature, tin oxide crystals may show in the microstructure. These are extremely hard, and the bronze is then difficult to machine.

Although the equilibrium diagram does not give any indication of a critical point for the α alloys, an improvement in properties is obtained by quenching, as the following results, due to Guillet,* for a bronze containing 95 per cent of copper and 5 per cent of tin will show:

Quenching Temperature.	Y.P.	M.S.	Elongation.
—	—	12·2	20·0
300° C.	6·5	15·2	27·5
550° C.	4·3	15·0	28·0
750° C.	4·7	12·2	22·0
800° C.	—	4·2	3·0

The sudden falling-off in both the ductility and strength when the alloy was quenched above 750° C. is very marked, and the best combination of properties was obtained by quenching at about 550° C.

Gun-metal.

Copper-tin alloys containing about 10 per cent of tin and about 2 per cent of zinc are known as gun-metals, since at one time they were extensively employed in ordnance work. From the brass and bronze diagrams already given it will be remembered that copper can hold 36 per cent of zinc in solid solution, but only about 14 per cent of tin if the alloys are to consist entirely of α solid solutions. The similarity which exists between the two α solid solutions leads to the formation of ternary α solid solutions.

By varying the composition of the ternary alloy either the γ brass or the δ bronze constituent may appear in the microstructure. Both these constituents are extremely hard and brittle. The γ brass constituent, however, tends to form at the crystal boundaries of the solid solution crystals, and the structure is then decidedly weak. On the other hand, the δ bronze constituent does not form continuous films, but exists in the form of rounded isolated masses; and, although the solid solution is very brittle itself, in this form it does not materially weaken the structure. Zinc is cheaper than tin, hence one reason for its introduction, but it is evident that an increase in the zinc content of a gun-metal may exert a much more harmful influence on its properties than a corresponding increase in the tin content. It is probably on this account that Admiralty specifications for gun-metal rigidly insist on a zinc content of less than 2·5 per cent.

Although zinc is cheaper than tin, this is not by any means the

* *Comptes Rendus*, 1905, Vol. CXL.

sole reason for its introduction into gun-metal. This metal acts as a powerful deoxidant, and so tends to prevent the formation of tin oxide. Zinc oxide is thus formed instead of tin oxide, but, since this is not a heavy material, it tends to rise to the surface of the molten metal much more readily than the heavier oxide of tin. Coinage bronze contains about 95 per cent copper, 4 per cent tin, and 1 per cent zinc, and in such material the zinc acts essentially as a deoxidant.

Zinc also increases the fluidity of gun-metal at any given temperature, and its introduction into copper-tin alloys leads to the production of much sounder castings. Zinc hardens bronzes, and thus counteracts the softening effect of the lead which is often added to these alloys to facilitate machining.

The addition of tin to copper results in greatly increased resistance to corrosion, and, as already indicated, the tensile strength is improved, although satisfactory ductility values are still obtained in the alloys containing up to 10 per cent of tin. Rolfe * gives the following tests as being the average of a large number of castings of Admiralty gun-metal (88 copper, 10 tin, 2 zinc):

Y.P.	M.S.	Elongation.
10·6	15·6	12·6

Gun-metal is chiefly employed for castings, and, if the best mechanical properties are to be obtained, particular attention must be given to the casting temperature. A very high casting temperature is to be avoided, and Carpenter and Elam † consider that the most satisfactory results are obtained when the alloys are cast at a temperature of about 1200° C. Better test values are obtained from sand than from chill castings. This might be expected, since in the latter case solidification is quicker and the chill-cast bronzes are liable to contain more of the α-δ eutectoid owing to the more pronounced coring.

H. S. and J. S. G. Primrose ‡ have shown that the properties of both sand and chill-cast gun-metals are improved by annealing at about 700° C. Some of their results are given in the following table:

	M.S.	Elongation.
Dry sand cast—slow solidification and moderately slow cooling	17·2	24·0
Dry sand cast and then annealed for ½-hour at 700° C. ..	18·0	37·5
Chill cast—rapid solidification and cooling ..	15·0	4·0
Chill cast and then annealed for ½-hour at 700° C.	20·0	30·0

* *J.I.M.*, 1918, Vol. XIX.   † *J.I.M.*, 1918, Vol. XIX.   ‡ *J.I.M.*, Vol. XXIII.

Just as with the pure copper-tin alloys containing 10 per cent of tin, the gun-metals should always be employed in the cast state for bearings.

Other Bronzes.

Alloys of copper and tin containing between 12 and 18 per cent of tin are frequently employed for bearings. A substitution of 2 to 4 per cent of zinc for copper is often made for such purposes. These alloys are heavily cored in the cast state and contain much of the α-δ eutectoid. The hard δ constituent tends to resist wear, but a series of microscopic channels are worn in the comparatively soft α, and this gives rise to a very effective system of lubrication.

In the alloys containing much less than 14 per cent of tin, prolonged annealing may result in an almost complete disappearance of the hard δ constituent, whilst in those containing more than 14 per cent of tin (the true α-δ bronzes) cavities may develop between the α crystals and the eutectoid areas, and persist after annealing. The hard δ constituent is then very loosely held in the α matrix, and tends to chip out very readily. In consequence, bearing bronzes of this type yield better results in the cast but very slowly cooled state.

Micrographs of a true α-δ bronze are shown in figs. 169 and 170.

The α-δ bronzes cannot be cold-worked on account of their composite nature and the presence in them of the hard brittle constituent. On heating to temperatures above 510° C., however, the eutectoid changes to the β solid solution, and the alloys are then much more ductile. Such materials can thus be worked at temperatures within the β or the α-β regions. Further, if quenched in water from temperatures above 510° C., the tendency is to retain the tough β solid solution, and the alloys may then be worked at ordinary temperatures. Advantage is sometimes taken of this fact in the hammering or beating of such articles as gongs, &c.

Lead-bronzes.

Lead is often introduced into bronzes to facilitate machining. Lead is practically insoluble in either the α or the β phases, and, in the solid bronze, exists in the form of globules. Up to 2 per cent of lead does not seriously affect the mechanical properties of either the true bronzes or the gun-metals, but higher proportions result in a very marked lowering of strength and ductility. Lead

Fig. 169.—Bronze containing 16 per cent of tin in the cast but slowly cooled state, cored α solid solution infilling the α-δ eutectoid. ×100.

Fig. 170.—The same bronze after being annealed at a comparatively low temperature. Islands of the eutectoid embedded in a matrix of homogeneous α solid solution crystals. ×100.
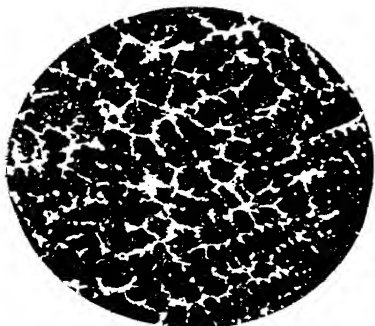
Fig. 171.—Phosphor-bronze containing 10 per cent of tin and 0·5 per cent phosphorus in a cast state. Copper-phosphide eutectic (light) in α matrix. ×100.

also lowers the resistance of such alloys to corroding influences; and, if considerable strength and resistance to corrosion are desired, this element must be kept below the above value.

Lead-bronzes are frequently employed for locomotive slide-valves and bearings. The lead exerts a softening effect on the alloys, which are then much more plastic, with the consequence that they are more quickly bedded to the journals. The addition of lead to a bronze helps it to resist wear, but does not increase its coefficient of friction. Alloys of this type contain between 5 and 10 per cent of tin, 8 to 10 per cent of lead, and up to 0·5 per cent of phosphorus. The latter element is added chiefly on account of its deoxidizing influence, with a consequent production of sounder castings.

The so-called *plastic bronzes*, containing up to 30 per cent of lead, have also been extensively employed for railway axle and other bearings where no considerable pressure is involved. Such bronzes generally contain about 5 per cent of tin. The chief difficulty in the manufacture of these alloys is in obtaining even distribution of the lead, since liquation may be very pronounced. The introduction of about 1 per cent of nickel tends to minimize liquation. The nickel gives rise to the production of a copper-nickel solid solution which freezes at a higher temperature than that at which the rest of the alloy commences to solidify, and this copper-nickel constituent thus forms a network throughout the semi-fluid bronze in which the particles of lead are entrapped. By this means a more even distribution of the lead is obtained, although the addition of nickel does not eliminate the necessity of a judicious adjustment of the casting temperature and vigorous stirring just before casting.

Phosphor-bronzes.

As already indicated, small amounts of phosphorus are often introduced into bronzes for deoxidizing purposes. These alloys are sometimes described as phosphor-bronzes, but the term is rather misleading, since in many instances the phosphorus content of the solid alloy may amount to traces only, and such small proportions have little or no effect on the properties of the bronze other than that due to more thorough deoxidation. The true phosphor-bronzes contain not less than 0·1 per cent of phosphorus, and the alloys having greater proportions than this exhibit very valuable properties. Thus the bronzes containing between 0·1

and 0·3 per cent of phosphorus, and not more than 5 per cent tin, may be readily cold-worked into rods, wires, and sheets. Parker * has suggested that alloys of this type are suitable for turbine blades, and considers that a maximum stress of at least 24 tons per square inch, and 13 per cent elongation, should be obtained on the material in the cold-worked state.

The tensile properties of an ordinary α bronze are considerably improved by the introduction of phosphorus, and the alloys exhibit a marked resistance to corrosion by sea-water.

Phosphor-bronzes with somewhat higher tin contents (10 to 13 per cent), and between 0·5 and 1 per cent of phosphorus, are employed for heavy duty bearings. These alloys are characterized by their low coefficients of friction, great hardness, and very pronounced resistance to wear. Bronzes with the lower tin and phosphorus contents are often used for valves, and the alloys rich in both tin and phosphorus for bearings and gears.

The microstructure of a true phosphor-bronze (fig. 171, facing p. 232) somewhat resembles that of a true α-δ bronze. Phosphorus is soluble in solid copper only to a very small extent, and, in a bronze, most of the element exists as copper-phosphide (Cu_3P), which forms a eutectic with the copper-phosphorus solid solution. This eutectic freezes at about 707° C., with the consequence that in the cast state it is entrapped between the arms of the α dendrites; and its disposition is then very similar to that of the α-δ eutectoid in a cast tin-rich bronze free from phosphorus.

Like the α-δ eutectoid, the copper-copper-phosphide eutectic is extremely hard and brittle.

The temperature of casting has a great influence on the microstructure and properties of phosphor-bronze, and should not exceed 1000° C. When properly cast, a phosphor-bronze has a tensile strength of about 14 tons per square inch, and it is worthy of note that the alloy retains its strength quite well at elevated temperatures, a maximum stress of 9 or 10 tons per square inch being obtained at about 450° C.

If cast at a high temperature and quickly chilled, the cored structure is very pronounced indeed, and the alloy may be too hard for machining owing to the presence of the eutectic and much of the α-δ eutectoid. Annealing may then be advantageous, since this not only tends to bring about absorption of the eutectoid, but may also yield better distribution of the eutectic.

* *J. Inst. Met.*, 1915, Vol. XIV.

Silicon-bronze.

Silicon is a powerful deoxidant, and very small amounts increase the strength and ductility of the bronzes to which it is added. Generally, only traces of the element are found in the solid alloys and the tin content is usually between 4 and 5 per cent. Such bronzes have high electrical conductivity, and are largely employed for telegraph and telephone wires.

Effect of other Elements on the Properties of Bronze.

Very small proportions of bismuth exert a very harmful effect on the properties of bronze. Less than 0·3 per cent of either antimony or arsenic does not appear to have any serious effect on the mechanical properties, but these elements are generally kept as low as possible. Iron hardens bronze, but may seriously lower its ductility.

Other Alloys of Copper

Copper-nickel Alloys.

The copper-nickel thermal equilibrium diagram is of the type given on p. 77, i.e. the metals form a continuous series of solid solutions, the melting-points rising progressively from that of copper (1083° C.) to that of nickel (1455° C.). All the copper-nickel alloys are cored in the cast state. The cored structure may be destroyed by annealing, although a very prolonged treatment is necessary with the alloys rich in nickel. After annealing, these materials are capable of withstanding considerable cold-work, and may be obtained in almost any desired shape or size. Annealing after cold-working results in the formation of innumerable and comparatively small twinned crystals.

Copper-nickel alloys are readily hot-worked, a property which enables them to be drop-forged.

The addition of nickel to copper results in a very marked change in colour, and when about 15 per cent of nickel has been introduced the alloys are almost white, maximum whiteness and brilliancy when polished being obtained with about 40 to 45 per cent of nickel.

Alloys containing about 2 per cent of nickel are employed for locomotive stay-rods and boiler and flue tubes. These materials in the cold-worked and annealed state have a tensile strength of

about 15 tons per square inch, and an elongation of about 50 per cent. They retain their strengths quite well at elevated temperatures, and also show a marked resistance to corrosion. Alloys containing from 10 to 12 per cent of nickel are employed in railway work where the water supply is distinctly corrosive.

Cupro-nickel, containing between 15 and 20 per cent nickel, is used for bullet envelopes, tubes, &c. Such alloys are characterized by their extreme malleability in the cold, and may be ranked amongst the most ductile of all the non-ferrous metals.
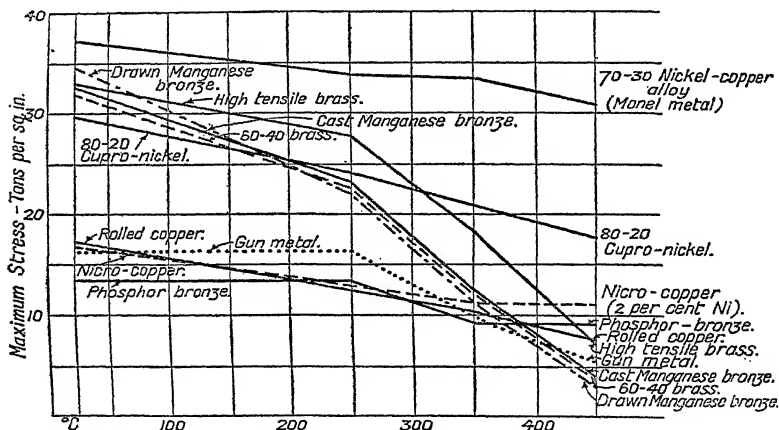
Fig. 172.—Tensile Strengths of Copper Alloys at Elevated Temperatures

In the annealed state these alloys have tensile strengths of 18 to 22 tons per square inch, with an elongation of about 40 per cent. The strength can be raised beyond 30 tons per square inch by cold-work. A comparatively recent application of 80–20 cupro-nickel is for marine and other condenser tubes. The alloys offer a very marked resistance to corrosion, and, what is of almost equal importance, they retain their strengths at elevated temperatures much better than most of the commercial brasses and bronzes (fig. 172). In addition, they do not appear to be liable to season-cracking.

Alloys containing between 40 and 45 per cent of nickel are readily cold-worked and, in the form of wire, find considerable electrical engineering application for rheostats, various kinds of

resistances, and thermocouples. These alloys, which are sold under the trade names *Constantan* and *Eureka*, are characterized by their comparatively high resistivities and their low resistance - temperature coefficients. The specific resistivity of constantan is about 50 microhms per cm.³. Cold-work does not greatly affect its resistivity, but Rohn * has shown that the temperature coefficient is affected to a very pronounced extent by cold-work. Great care must therefore be exercised in making up resistances with these alloys, and stretching avoided. Thermocouples consisting of one wire of constantan with another wire of either copper, iron, silver, &c., are characterized by their comparatively large E.M.F.s, and are amongst the most satisfactory of the " base-metal " thermocouples.

Copper-nickel alloys containing about 70 per cent of nickel constitute what is known as *Monel metal*. This is produced by the smelting of a nickel ore containing copper, the two elements being present in the ore in about the same proportions as those in the final product, and the alloy can therefore be produced more cheaply than the synthetic alloys made from copper and nickel. The simple method of manufacture affords little control over the composition of the product, however, and consequently the physical properties of Monel metal vary somewhat. The alloys generally contain from 0·5 to 4 per cent of iron, from traces to 2 per cent of manganese, and smaller but definite proportions of silicon, zinc, carbon, sulphur, and phosphorus.

One of the most striking characteristics of Monel metal is its very pronounced resistance to corroding influences. It resists attack by sea-water, superheated steam, alkalis, salt solutions, oils, aromatic compounds such as phenol and cresol, and many fatty and other organic acids. In consequence, the material finds considerable application in marine and chemical engineering.

Monel metal offers little or no resistance to attack by mineral acids, ferric iron solutions, cyanide solutions, chromic acid, or molten lead or zinc.

In view of the fact that the composition of Monel metal is somewhat indefinite, it is difficult to give typical test values. The alloys are, however, much stronger than most other non-ferrous alloys, not excluding the high tensile brasses.

Both chill and sand castings may be made from Monel metal. Sound castings are obtained by using manganese as a deoxidant,

* *Z. für Metallkunde,* 1927, Vol. XIX.

a small amount of magnesium (about 0·15 per cent) being added just before casting to render the deoxidation as complete as possible. Sand castings cooled at a moderately slow rate will give a tensile strength of about 30 tons per square inch and an elongation of 25 to 35 per cent.

Monel metal is readily hot-worked, but the best temperature range for the forging down of ingots and for hot-rolling is from 1050° and 1150° C. The alloys can be cold-drawn and cold-rolled into sheets and wire, but annealing is necessary if the reduction in cross-section exceeds 90 per cent. During annealing the formation of much oxide on the surface must be avoided, since, owing to their very marked corrosion-resisting properties, oxide films are only removed with difficulty. In a pamphlet published by the International Nickel Company, the following pickling solution is recommended for improving and brightening the surface of Monel metal having a superficial oxide coating:

> Sulphuric acid, 10 per cent.
> Sodium or potassium dichromate, 1·0–2·0 per cent.
> Water, 88·0–89·0 per cent.

The mechanical properties of the cold-worked material obviously depend on the degree of cold-work to which it has been submitted, as will be evident from the following data obtained on a 70 per cent nickel alloy:

Per Cent Reduction by Cold-rolling.	M.S., tons/sq. in.	Elongation, per cent.	Brinell Hardness.
22·5	38·1	11·5	186
57·2	47·7	5·8	208
91·4	59·9	2·3	256
91·4 and then annealed at 700° C. for ½-hour	30·0	39·7	—

Monel metal retains its strength to a very appreciable extent at elevated temperatures, and has a creep limit of about 10 tons per square inch at 500° C. Its resistance to corrosion and comparatively high tensile strength at elevated temperatures have resulted in its application for such purposes as valves, turbine blades, and other parts which are in contact with steam at high pressures. In addition, the alloy is widely employed for condenser tubes in high-pressure marine work.

Effects of Impurities on the Properties of the Copper-nickel Alloys.

Great care is necessary in the manufacture of copper-nickel alloys in order to minimize oxide formation, since if much oxide is present in the solid alloys both the tenacity and ductility may be very seriously affected. Deoxidation is generally carried out by the addition of 0·2 to 1 per cent of manganese just before casting.

Sulphur is a probable impurity in copper-nickel alloys, and particularly in those melted in coke-fired furnaces. Sulphur exerts a definite embrittling effect on the materials, and is therefore kept as low as possible by rapid melting and quick casting.

All the commercial copper-nickel alloys contain small proportions of carbon. In castings which are cooled moderately quickly the carbon exists in solid solution, and in this form increases the strength of the castings. In castings which are not to be submitted to any form of heat-treatment the presence of carbon is rather advantageous, since it not only confers increased strength, but also acts as a deoxidant and ensures freedom from oxide. In such materials, however, 0·25 per cent of carbon is regarded as a maximum limit.

In the copper-nickel alloys which are to be forged and rolled and subjected to an annealing treatment, the proportion of carbon is generally kept below 0·1 per cent. Annealing may result in the decomposition of nickel carbide and the precipitation of carbon as graphite. This may be formed along the crystal boundaries, and lowers the strength of the alloys and tends to make them porous; the graphite particles tend to initiate corrosion, and the surfaces of the finished articles are not so satisfactory.

If necessary, the annealing of an alloy after it has been cold-worked should be carried out at as low a temperature as possible, since higher temperatures tend to promote rapid graphitization of any carbon that may be present in the alloy. Further, annealing should be carried out in a non-oxidizing atmosphere, since otherwise a very tenacious covering of scale is produced on the surface which is only removed with great difficulty.

The Mechanical Properties of Copper Alloys at Elevated Temperatures.

The influence of temperature on the mechanical properties of copper alloys has been studied by several workers. The results

obtained indicate that all the nickel-copper alloys retain their strengths very well at elevated temperatures, and to a more pronounced degree than the high-tensile brasses, phosphor-bronzes,

Fig. 173.—Showing Relation between Tensile Strength and Limiting Creep Stress for a 70–30 Nickel-copper Alloy

and gun-metals, although these alloys may possess higher tensile strengths at ordinary temperatures. The curves given in fig. 172 (p. 236) have been plotted from data obtained from several sources and published in a pamphlet issued by the Bureau of Information on Nickel.* Creep-time curves for cupro-nickel have already been given on p. 187. Tapsell and Bradley † have carried out exhaustive tests on a copper-nickel alloy containing 28·16 per cent copper, 68·74 per cent nickel, 2·35 per cent manganese, and 0·56 per cent iron. Some of their results are plotted in fig. 173.

Copper-nickel-zinc Alloys.

These alloys are generally known as *German silver* or *nickel-silver*, although comparatively recently the term *nickel-brass* has been applied to such materials since it serves to indicate their constitution more accurately. The nickel-silvers do not contain silver and may be regarded as brasses to which nickel has been added.

These alloys have a pleasing appearance and take a brilliant finish. Those of the greatest engineering importance contain between 20 and 30 per cent of nickel, and the best qualities have their copper and zinc contents in about the same relative proportions as those in a 70–30 brass. The higher the nickel content the whiter is the colour.

The compositions vary considerably, but all the useful alloys fall into the α solid solution region of the Cu-Ni-Zn ternary system,

* Publication R.2.—Nickel-copper alloys containing more than 50 per cent nickel, March, 1930.   † *J. Inst. Met.*, 1926 (i).

and their metallography is comparatively simple in consequence. In the cast state, even when very slowly cooled, the nickel-silvers are heavily cored, and the coring, which is most pronounced in the alloys richest in nickel, is very persistent, and is never completely obliterated by working and annealing. The alloys may be readily cold-worked, but annealing is necessary at intermediate stages. As with all the α solid solutions, such treatment yields innumerable twinned crystals, but if drastically " over-annealed ", the twins may be obliterated; and if the overheating is carried to an extreme degree incipient fusion may occur, a variant of the cored structure being reproduced in consequence. Further, as in the brasses, overheating may cause volatilization of some of the zinc with the formation of intercrystalline cavities.

For a given treatment the size of the crystals decreases with increasing nickel content, and the alloys are stronger, as shown by the following test results:

Condition.	Nickel, per cent.	Copper, per cent.	Zinc, per cent.	M.S., tons/sq. in.	Elongation, per cent.
Annealed	10	62	28	28·0	48
	18	55	27	30·8	29
	25	55	20	31·5	38
	30	47	23	32·5	32

Cold-work increases the strength of nickel-silver but lowers its ductility, and in the higher nickel alloys a maximum stress between 55 and 60 tons per square inch may be obtained by cold-working.

The temperature necessary for full annealing depends on the composition of the alloy. In practice temperatures between 650° and 750° C. are employed, the higher temperatures being applied with alloys of the higher nickel contents. On no account should the temperature exceed 800° C.

The nickel-silvers offer a very pronounced resistance to corroding influences.

The alloys find considerable engineering application. They are used for automobile radiator shells, motor-car, railway carriage, marine, and sanitary fittings, valves, ornamental fixtures, and in the form of tape and wire for electrical resistances.

The usual precautions must be taken in preventing oxidation during melting and casting. A small proportion of manganese is generally used as a deoxidant, and if the best results are to be obtained for both ingots and castings the pouring temperature must be carefully controlled. The best casting temperature for a 16 per cent nickel alloy is about 1250° C., a temperature about

100° C. higher being employed for an alloy containing about 30 per cent nickel.

The machining properties of nickel-silver castings are greatly improved by the introduction of about 2 per cent of lead. Lead lowers the strength of the alloy, and, in particular, its ductility and malleability. If much lead is present the alloys are unsuitable for cold-working.

The specific resistance of nickel-silver increases with increasing nickel content, and the following relationship, due to Thompson, gives very close approximations to the observed values:

Nickel per cent $+$ 12 $=$ Specific resistance in microhms per cm.^{3}.

The temperature coefficient of resistance also varies with the nickel content, being about 0·00076 and 0·00021 per 1° C. for the alloys containing 7 and 30 per cent nickel respectively.

Copper-nickel-zinc alloys are employed for brazing purposes. For nickel-silver, alloys containing 8 to 12 per cent of nickel, 40 to 50 per cent zinc, and 35 to 45 per cent of copper may be used. The alloys richest in zinc are the most fusible, but a high proportion of zinc may lead to the presence of much of the γ brass constituent in the brazed joint, which is very brittle in consequence.

Alloys of somewhat higher copper contents (45 to 50 per cent), lower zinc, and about 10 per cent of nickel are sometimes employed for brazing iron and steel.

Alloys of Copper and Aluminium.

Copper and aluminium give rise to two really remarkable series of alloys—those rich in copper and those rich in aluminium. The intermediate alloys are of no engineering importance.

The alloys rich in aluminium will be considered in a subsequent chapter. That part of the diagram relating to the alloys rich in copper which are of industrial importance is given in fig. 174. These alloys are known as the *aluminium bronzes,* although they do not contain tin. It will be seen that aluminium is soluble in solid copper to the extent of 9·8 per cent at ordinary temperatures. Alloys containing less than this yield a series of α solid solutions possessing the general characteristics of such a series. Thus these alloys are heavily cored in the cast state, although the distance between liquidus and solidus is not great. The coring disappears completely with prolonged annealing, and the materials may be worked either hot or cold. Alloys containing from 5 to 7

per cent of aluminium have a very pleasing appearance and a colour similar to that of 18 carat gold. The tensile strengths of these alloys are relatively high, and they exhibit a useful resistance to corrosion.

In the cast state such materials will yield the following tensile test results:

Y.P., tons/sq. in.	M.S., tons/sq. in.	Elongation, per cent.
4·0–6·0	18·0–20·0	65·0–75·0
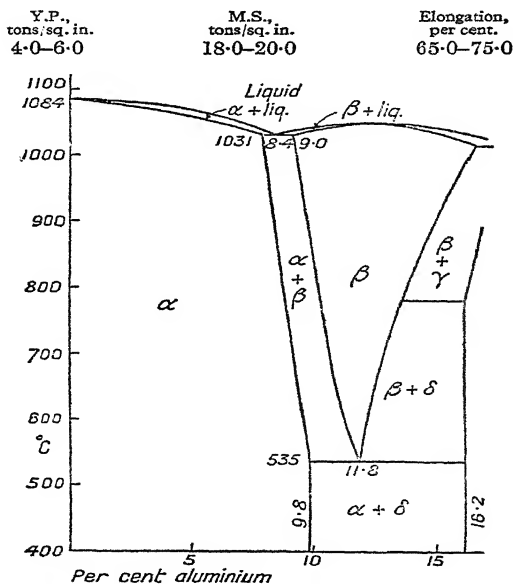
Fig. 174.—Thermal Equilibrium Diagram for Copper-rich Copper-aluminium Alloys

Cold-working increases the strength but lowers the ductility, and the latter may be restored by annealing as shown by the following data, due to Rosenhain and Hanson,* for an alloy containing 7 per cent of aluminium.

	Y.P.	M.S.	Elongation.	Brinell No.
Hard-rolled	38·7	39·8	17·5	195
Hard-rolled and then annealed at 650° C. ..	7·0	27·5	71·0	75·5

The low yield-point values for these alloys should be noted

* *J. Inst. Met.,* 1929 (i), Vol. XXI.

Alloys containing the foregoing proportions of aluminium are employed for domestic and decorative purposes, seamless tubing, wire, &c.

At a temperature just above 535° C. an alloy containing between 9·8 and 11·8 per cent of aluminium consists of primary α solid solution crystals and the β solid solution containing about 11·8 per cent of aluminium. At this temperature, however, the β crystals break down into a eutectoid of α and δ saturated solid solutions containing 9·8 and 16·2 per cent of aluminium respectively. The β solid solution is therefore stable only at temperatures above 535° C.

The δ solid solution is a very hard material, and alloys containing it possess considerably higher tensile strengths than the α alloys of lower aluminium content. The δ constituent is very brittle, however, and alloys containing more than 11 per cent of aluminium have little or no ductility; the industrial alloys do not generally contain more than 10 per cent of the element.

Alloys containing from 9·8 to 11·8 per cent of aluminium are susceptible to heat-treatment, and are· of great interest, since that part of the diagram involved offers the closest analogy to the " steel " panel of the iron-iron-carbide diagram. Thus, in the slowly cooled alloys, the α-δ eutectoid has a distinctly lamellar appearance like that of pearlite in steel. The boundaries of the wholly β solid solution region meet at a eutectoid point corresponding to 11·8 per cent of aluminium, and the β region may be compared with that of the austenite region of the iron-iron-carbide system; the α-β region corresponding to that of the ferrite-austenite part, whilst the area below 535° C. is the analogue of the ferrite-pearlite region.

In the cast state, Widmanstätten structures are obtained just as with medium and low carbon steels. Annealing at temperatures just inside the β region destroys the Widmanstätten pattern, and if the alloy is slowly cooled, the resulting microstructure consists of islands of α in a pearlitic matrix. Annealing lowers both the strength and the ductility, and is not recommended for industrial purposes.

If an aluminium bronze containing, say, 10 per cent of aluminium is quenched from the β region, its microstructure has a decidedly martensitic appearance. No constituent corresponding to troostite is apparent, but if the quenched specimens are tempered, small particles of the δ solid solution are evenly disseminated throughout the mass, and the material then has a structure comparable with
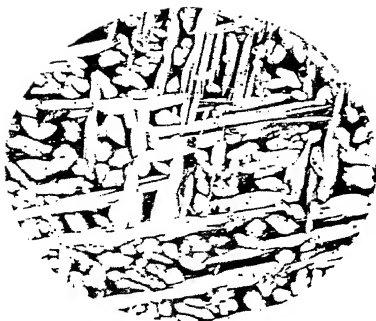
Fig. 175. — Aluminium bronze containing 10·5 per cent aluminium in cast but slowly cooled state. a, light; a-δ eutectoid, dark. Vickers hardness 127. × 100.

Fig. 176.—The same alloy heated to a temperature within the β region and quenched in water. a needles in β matrix. Vickers hardness 258. × 100.
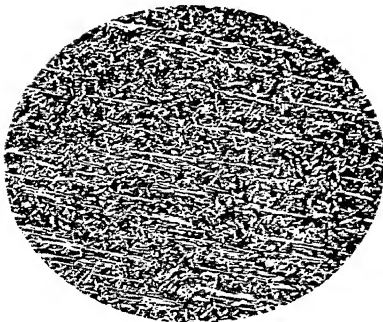
Fig. 177.—The same specimen after being tempered at 500° C., sorbite structure consisting of an intimate mixture of a and δ. Vickers hardness 164. × 100.
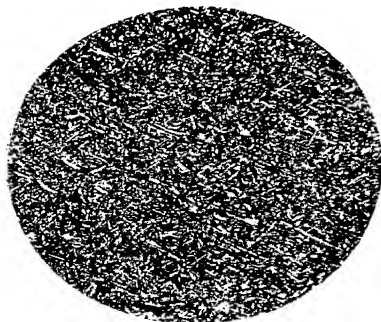
that of sorbite in a quenched and tempered steel. The hardness of quenched specimens falls away as the tempering temperature is increased.

The effects of different treatments on the microstructures of a 10 per cent aluminium alloy are clearly shown in figs. 175, 176, and 177, and the influence on the mechanical properties is illustrated by the following data:

Condition.	Y.P.	M.S.	Elongation.	Reduction of Area.
Chill-cast	13·4	36·2	22·5	22·5
Quenched 900° C. in water	19·6	43·2	1·5	1·0
Quenched 900° C. and tempered 650° C. ..	17·6	38·6	24·0	21·5

Alloys of the above composition are often employed for purposes where steel is unsuitable and a fair strength is required, such as pump-rods, &c., and for castings which have to withstand considerable pressure.

The material is also employed for die-castings, some of which are of rather intricate design. For such purposes alloys containing about 10 per cent of aluminium, from 1 to 3 per cent of iron, and small proportions of manganese are generally preferred.

The alloys retain their strengths at high temperatures, and at 300° C. a 10 per cent aluminium alloy has a maximum stress of about 33 tons per square inch.

Alloys containing about 10 per cent of aluminium and from 1 to 1·5 per cent of nickel are now being employed for exhaust valve seats of internal-combustion engines. For this purpose the material is quenched in water and then tempered so as to give a Brinell hardness between 190 and 230, which corresponds to a tensile strength of more than 40 tons per square inch.

Aluminium and its Alloys.

Aluminium is the most abundant of all metals, and its compounds containing the oxide Al_2O_3 form a very considerable part of the earth's crust. Until modern times, however, the metal was unknown in the free state, a consequence of its extraordinary affinity for oxygen. The production of aluminium from its oxide is difficult, since the reduction cannot be effected by means of either carbon or hydrogen.

The whole of the world's supply of aluminium is now produced by electrolytic processes, and it was not until the advent of the

modern electric arc furnace that the production of aluminium on a commercial scale became at all possible.

The only naturally occurring mineral suitable for electrolytic reduction is a hydrated form of the oxide known as bauxite. This material is frequently contaminated with iron oxide and silica, and these substances also undergo electrolytic reduction, with the consequence that the final product may contain appreciable amounts of iron and silicon. Metallic aluminium cannot be easily purified, so that if the ore contains much impurity a commercially pure product can only be obtained by purification of the ore before it is subjected to the electrolytic process. Silicon is a most troublesome impurity to remove. All commercial aluminium contains from 0·5 to 1·5 per cent silicon, and somewhat lower but appreciable amounts of iron.

The electrolytic process which is employed is known as the Hall process. Pure aluminium oxide does not conduct electricity, and cryolite—a double fluoride of sodium and aluminium—is employed as an electrolyte and solvent for the oxide. Molten cryolite will dissolve about 25 per cent of the oxide at 900° C. The freezing-point of the cryolite mixture is progressively lowered by additions of oxide, and a further depression of the freezing-point and a greater degree of fluidity at the working temperature (850°–900° C) is obtained by the addition of sodium and calcium fluorides. Only the dissolved oxide of aluminium undergoes electrolytic reduction, the other substances being unaffected. Direct current is employed, and enters the furnace through carbon electrodes, the carbon lining of the furnace constituting the cathode. The oxygen produced by the electrolysis burns away the anodes to yield oxides of carbon, whilst the metallic aluminium, which is heavier than the electrolyte, sinks to the bottom of the furnace, from which it is withdrawn at suitable intervals and cast into notched ingots.

Properties of Commercial Aluminium.

Aluminium is a soft white metal, and is one of the lightest metals known. The specific gravities of common commercial metals and alloys are given in the following table:

Magnesium	..	1·75	Tin	..	7·3	Copper	..	8·8
Aluminium	..	2·68	Steel	..	7·8	Nickel	..	8·9
Cast iron	..	7·2	Brass	..	8·4	Lead	..	11·3
Zinc	..	7·2	Bronze	..	8·6			

It is on account of the low density of aluminium and its most important alloys that this metal is employed in engineering.

Aluminium is a good conductor of heat and electricity. Its specific electrical conductivity is about 60 per cent of that of copper, but weight for weight it is a better conductor than copper, and it is therefore being employed for cable purposes. Aluminium is such a weak metal, however, that it is necessary to reinforce the cable with a central core of thin steel wire.

Alloys of aluminium are also being extensively employed for overhead cable work. One such alloy, known as *Aldrey*, contains about 0·5 per cent magnesium and 0·7 per cent of silicon, the remainder, apart from the usual iron impurity, being aluminium. About 0·5 per cent of manganese is used as a deoxidant. This material and its related alloys possess the advantage that the tensile strength, in the heat-treated condition, is about twice that of pure aluminium. According to Zeerleder and Bosshard * the wires are heat-treated during drawing by heating to 570° C., quenching in water, and then " ageing " for a prolonged period.

The electrical conductivity of Aldrey is about 80 per cent of that of pure aluminium, and the alloy exhibits a useful resistance to corrosion.

The thermal conductivity of aluminium is about 0·55 C.G.S. units at ordinary temperatures as against values of 0·92 and 0·17 for copper and iron respectively.

Mechanically, aluminium is a very weak metal, and in the cast state has a tensile strength of from 6 to 7 tons per square inch only, with an elongation of about 3 per cent. Its poor properties render it unsuitable for castings and for purposes where strength is required. The metal may, however, be readily worked either hot or cold, and its mechanical strength may be raised by cold-work to about 12 tons per square inch. The material may be completely softened, after cold-working, by annealing between 350° and 400° C.; and although this lowers the strength to about the same as that of the original unworked metal, a considerable improvement in the ductility is obtained, the elongation being about 40 per cent.

About half the total aluminium produced is employed for sheets, wire, rods, &c., practically the whole of the remainder being used in the manufacture of light aluminium alloys. The metal is also employed in the manufacture of the misnamed

* Z. für Metallkunde, 1927.

" aluminium bronzes ", and is used in powder form in aluminium paints and sprays.

On heating, aluminium readily oxidizes, and its oxidation is strongly exothermic. The metal and its alloys offer a marked resistance to ordinary atmospheric corrosion, however, a fact which is attributed to the formation of exceedingly thin protective films of oxide on their surfaces. Aluminium is readily attacked by caustic alkalis, acids, and salt solutions, and its tendency to corrosion is markedly increased by the proportion of impurities, notably iron, in it.

Alloys of Aluminium.

Commercially pure aluminium has very poor machining properties, it tears badly, and will not take fine threads; and this, together with its poor mechanical properties, renders the metal unsuitable for many engineering purposes. The introduction of small proportions of other elements, however, leads to a very marked improvement in mechanical properties and machinability. Thus the well-known and widely used aluminium alloy " duralumin ", which contains about 4 per cent of copper and smaller proportions of other elements, is as strong as mild steel, is easily machined, and will take a micro-thread. Although in most cases these other elements raise the specific gravity, the alloys are still relatively light, and in the most useful alloys the density is less than 3. The extreme lightness and fair strength of the alloys of aluminium is of distinct advantage in certain engineering problems, since it permits the use of a larger volume with a consequent increase in the rigidity of the structure without increasing its weight.

In other cases, such as, for instance, the pistons and connecting-rods of internal-combustion engines, where the mass of the moving parts must be as low as possible, the use of the stronger light aluminium alloys has proved to be extremely beneficial. In such instances a further advantage is obtained by the employment of aluminium alloys in view of their relatively high thermal conductivities. Griffiths and Schofield * give the value 0·39 C.G.S. units as the average thermal conductivity of 20 aluminium alloys at 0° C., mean values for steel and cast iron being about 0·11 and 0·052 respectively. Further, the temperature coefficients of thermal conductivity for the last two materials have a negative sign, whereas positive values are obtained for aluminium and its alloys, and the

latter thus become better conductors of heat at elevated temperatures.

The coefficient of linear expansion of a light aluminium alloy depends on its composition and on the temperature range considered, but values between 0·000022 and 0·000027 are generally obtained. The values for steel and cast iron are 0·000011–0·000015 and 0·000008–0·000014 respectively. This great difference in expansibility must be considered when an aluminium alloy piston working in a cast-iron cylinder is employed, since if sufficient clearance is not allowed between the piston and the cylinder wall seizure may occur. One very ingenious way of overcoming this difficulty consists in the use of " Invar " struts across the piston. By this means the net lateral expansion of the piston may be made to approximate very closely to that of the cast iron, and a satisfactory and almost constant clearance can therefore be maintained under all working conditions.

Many of the aluminium alloys are employed in the form of castings. Since in many cases these are of somewhat thin and intricate section, casting stresses, unevenly developed, are readily developed in them. The release of such stresses, during service, in parts which are not heat-treated after casting, may cause distortion. If, however, the material is annealed at a temperature of 350°–420° C. after it has been machined, warping is eliminated altogether

The useful light aluminium alloys may be divided into several classes, according to their chemical composition, as follows:

(a) Alloys containing copper, with or without magnesium.
(b) Alloys containing zinc and copper.
(c) Alloys containing silicon, with or without copper.

Most of these alloys are covered by the specifications of the British Engineering Standards Association under designations which, in some cases, will be referred to in subsequent paragraphs.

Aluminium-copper Alloys.

Of the straight copper alloys only two types need be considered, those known as 3L11 and 2L8 containing 6–8 and 12 per cent of copper respectively. These alloys have been extensively employed for castings, the 12 per cent copper alloy having found considerable application for pistons since it possesses a fair strength at elevated temperatures.

The alloys are susceptible to heat-treatment, and that part of the thermal equilibrium diagram involved is given in fig. 178. It will be observed that copper and aluminium yield an intermetallic compound having the formula $CuAl_2$ which is soluble in excess aluminium to yield the ζ solid solution. The homogeneous ζ solid solution region is confined within comparatively narrow limits. At the aluminium end of the diagram θ solid solutions are obtained, and it will be noticed that the copper concentration of the saturated θ solution is greater at higher than at lower temperatures. The solubility of copper in aluminium at 548° C. is about 5·6 per cent, but at ordinary temperatures the solubility is only about 0·3 per cent.

The above two solid solutions give rise to the formation of a eutectic containing 33·8 per cent of copper, and consisting of the ζ and limiting θ solid solutions. Alloys containing between 5·6 and 33·8 per cent of copper thus consist of primary θ solid solution crystals and eutectic.

Fig. 178.—Aluminium End of the Copper-aluminium Thermal Equilibrium Diagram

In the cast state these alloys are always cored, with the consequence that the proportion of the eutectic is greater than the theoretical. As such an alloy cools, the copper concentration of its θ solid solution decreases, and more of the ζ solid solution is deposited.

Consider now the reheating of an alloy containing, say, 6 per cent of copper. During heating diffusion occurs, the coring is obliterated, with the consequence that most of the eutectic disappears, and if the alloy is taken up to about 530° C. the concentration of the θ solid solution is such that very little of the $CuAl_2$ (ζ) solid solution remains undissolved. If the alloy is quenched from this temperature a supersaturated θ solid solution is retained at ordinary temperatures. This supersaturated solid solution is

unstable, and if the alloy is " aged ", i.e. kept at room temperatures for several days, it deposits the $CuAl_2$ solid solution in the form of ultra-microscopic particles, the $CuAl_2$ which remained undissolved acting as nuclei for the decomposition. This reprecipitation is accompanied by a marked alteration in the physical properties of the alloy, and its strength and hardness increase. Although at ordinary temperatures several days elapse before the ageing phenomenon is complete and maximum hardness is developed, complete ageing may be accomplished by tempering the alloy after quenching, at 100° C. (in boiling water) for a period of about six hours.

Age-hardening is now recognized as being of general occurrence in all systems where a rise in temperature involves an increase in solid solubility. The phenomenon will again be referred to in connexion with the well-known duralumin and " Y " alloys.

The properties of the copper-aluminium alloys already quoted are as follows:

Name and Condition.	Specific Gravity.	Y.P.	M.S.	Elongation.	Brinell No.	Izod Impact.
3L11 (6–8 per cent copper) as cast ..	2·8–2·84	4–8	10–12	3–6	54–64	2–5
2L8 (11–13 per cent copper) as cast ..	2·9–2·96	6–7	11–14	1·5–2·5	74–87	1·0–2·5
6 per cent copper alloy " heat-treated ", i.e. quenched and aged	2·82	9·5	21	13	95	8

Duralumin.

The remarkable alloy " duralumin " was first developed by Wilm in 1911. This material is susceptible to heat-treatment, and in the heat-treated condition possesses unique physical properties. Although its density is little more than that of pure aluminium, it has a tensile strength of more than 20 tons per square inch in the treated condition, and has good machining properties.

The B.E.S.A. specification for duralumin is 3·5–4·5 per cent copper, 0·4–0·7 per cent manganese, 0·4–0·7 per cent magnesium, about 0·4 per cent silicon, and not more than 0·5 per cent of iron. The following composition is quite typical: copper, 3·7 per cent; manganese, 0·61 per cent; magnesium, 0·43 per cent; zinc, 0·25 per cent; silicon, 0·58 per cent; iron, 0·53 per cent; aluminium, 93·9 per cent. The iron and silicon are not intentionally added, but are present in the aluminium as impurities. Every effort is

made to keep the iron as low as possible; and, as indicated above, some specifications insist on an iron content below 0·5 per cent, since higher proportions exert a detrimental influence on the properties of the heat-treated alloys. Silicon, although in reality an impurity, is considered by some authorities to be essential for effective ageing.

It has been shown that in alloys containing magnesium much of the silicon exists in the form of a very stable silicide of magnesium having the formula Mg_2Si. This compound with aluminium yields a thermal equilibrium diagram which, at its aluminium end, closely resembles that for the copper-aluminium alloys rich in aluminium (fig. 179). Thus saturated solid solutions of Mg_2Si in aluminium are formed, the concentrations increasing at elevated temperatures, and a eutectic occurs at 580° C., consisting of the excess Mg_2Si and the limiting solid solution. The microstructure and its relation to the properties of duralumin can therefore be considered from the two binary systems involved.

Fig. 179.—Equilibrium Diagram: Aluminium-Mg_2Si

The copper content of duralumin is generally about 4 per cent. Theoretically, therefore, the whole of the copper should be present in the θ solid solution at temperatures above 500° C. The alloys are always cored in the cast state, however, with the consequence that some eutectic is generally present as infilling. As the solid alloy cools the θ solid solution crystals also deposit some of the $CuAl_2$ solid solution within them.

Magnesium silicide behaves in a similar manner, with the consequence that cast specimens of duralumin consist of cored solid solution crystals with some eutectic—containing both $CuAl_2$ and Mg_2Si—at the crystal boundaries. The structure of a specimen of cast duralumin is given in fig. 180, and although its constituents are not readily identified in the micrograph they are easily distinguished under the microscope. Thus in the etched specimens

Fig. 181.—Specimen taken from forged duralumin propeller; the cast structure has been broken down. Vickers hardness 61. ×200.
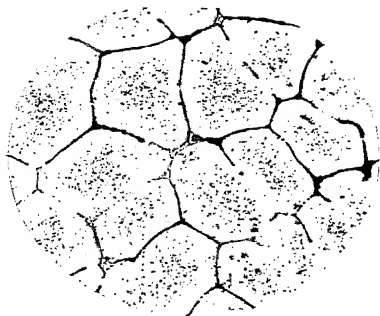
Fig. 180.—Duralumin in the cast state. $CuAl_2$ (dark) and Mg_2Si (half-tone) constituents at the boundaries of the θ solid solution crystals. Vickers hardness 90. ×200.

Fig. 182.—The same specimen after heat-treatment and ageing. Note the difference in the appearance of the matrix. Vickers hardness 119. ×200.

Fig. 183.—Specimen of identical composition quenched from 510° C. and then aged. Overheating has produced a material having large crystals and massive areas (black) of the $CuAl_2$ constituent. Vickers hardness 102. ×200.

[*Facing p.* 252

the Mg_2Si appears as a grey or bluish-grey constituent, and the $CuAl_2$ solid solution is coloured dark-brown or black. The iron constituent which is always present in commercial aluminium alloys has a brilliant appearance, whiter even than the θ solid solution itself.

Duralumin is not suitable for the production of castings, but large quantities are employed in aeronautical and automobile engineering in the form of forgings, stampings, bars, sheets, tubes, rivets, &c. The alloy is readily hot-worked by heating to a temperature of about 500° C. During the reheating for forging the eutectic disappears and the coring is obliterated (fig. 181).

After forging or annealing, duralumin may be cold-worked to quite an appreciable degree, and a combination of both hot- and cold-working is indeed generally employed for the production of sheets, &c. The alloy is obtained in the fully softened state by annealing at about 400° C.

Duralumin exhibits the phenomenon of age-hardening to a very pronounced degree. If the alloy is heated to about 480° C. and quenched in water, its properties differ little from those of the untreated material, but subsequently its hardness increases, rapidly at first, and then more slowly, up to a maximum value after a period of about four or five days.

The age-hardening process may be considerably accelerated and completed in a few hours by reheating the quenched alloy in boiling water, or some other medium, so long as the temperature does not exceed 150° C. If higher ageing temperatures are employed the material is much too soft. On the other hand, if quenched from above 490° C., and afterwards subjected to a correct ageing treatment, the product may not be sufficiently ductile, since the first heating results in the re-formation of some eutectic which persists. The microstructure of an overheated but correctly aged specimen of duralumin is shown in fig. 183. The large crystal size and the massive areas of the $CuAl_2$ constituent are readily shown. The structure approximates that of the cast material and the specimen was brittle in consequence, although its hardness was considerably lower than that of the correctly treated material. The quenching temperature was 510° C., and thus the necessity for accurate temperature control and the frequent calibration of pyrometers is clearly shown. Further, it should be realized that such a structure greatly lessens the resistance of the material to corroding influences.

If the temperature from which the alloy is quenched is much below 480° C., comparatively large particles of $CuAl_2$ and Mg_2Si are never taken into solution, and are present in the final product, with the consequence that its resistance to corrosion is much less marked.

Aged duralumin is capable of withstanding quite an appreciable amount of deformation by cold-work.

The cause of the age-hardening of duralumin has been a very controversial matter in the past. On heating, both the $CuAl_2$ and Mg_2Si dissolve in the aluminium, and, on quenching, a supersaturated solution of both compounds in aluminium is retained at ordinary temperatures. This supersaturated solution breaks down in time, depositing both the dissolved substances in a highly dispersed state; but whilst the U. S. Bureau of Standards attribute the age-hardening phenomenon solely to the deposition of particles of $CuAl_2$, the National Physical Laboratory consider that the precipitated Mg_2Si is the more effective agent, since it was observed that alloys low in copper and free from magnesium showed little or no tendency to age-harden. It has been suggested that the particles of Mg_2Si are first formed, and that these then act as nuclei for the rapid breakdown of the remaining supersaturated solid solution containing $CuAl_2$.

The particles of Mg_2Si and $CuAl_2$ in a correctly treated specimen of duralumin are in a highly dispersed state, and cannot be observed under the microscope. If higher ageing temperatures than 150° C. are employed, the particles coalesce and are rendered visible, but by the time this occurs the point of maximum hardness has been passed and the alloy is not in its most satisfactory condition.

The structures of forged and heat-treated duralumin are shown in figs. 181 and 182. Typical test results are as follows:

Condition.	Y.P.	M.S.	Elongation.	Reduction of Area.	Brinell No.
Air-cooled from 500° C. ..	7	18	21	44	65
Quenched in water from 500° C.	7	17	20	41	63
Quenched and aged ..	15	26	20	35	98

The density of duralumin is about 2·8, its coefficient of linear expansion is about 0·000023 per 1° C., and its thermal conductivity about 0·3 C.G.S. units.

Duralumin retains its strength fairly well up to 200° C., and at this temperature has a tensile strength of about 20 tons per square inch. The strength rapidly falls off at temperatures above 200° C

" Y " Alloy.

Y alloy was developed by the National Physical Laboratory, and has the following composition: copper, 4 per cent; magnesium, 1·5 per cent; nickel, 2 per cent. Apart from smaller proportions of iron and silicon as impurities, the remainder of the alloy consists of aluminium.

Like duralumin, Y alloy may be mechanically worked, and is sometimes employed for forgings. Unlike duralumin, however, it is chiefly used for castings. In order to obtain the best combination of physical properties the alloy must be subjected to a form of heat-treatment similar to that employed for duralumin, although a somewhat higher quenching temperature (510°–520° C.) is necessary, and the ageing is carried out at room temperatures over a period of about five days.

Typical test values are as follows:

Condition.	Specific Gravity.	Y.P.	M.S.	Elonga-tion.	Brinell No.	Impac
As cast	2·79	10—11	12—14	2	82—85	1
As cast and heat-treated	2·78	14—16	18—22	4—6	96—105	3—5
Hot - worked and heat-treated ..	2·79	14	22	15	105	—

The properties of Y alloy are thus much the same as those of duralumin. Y alloy retains its strength somewhat better at elevated temperatures, however, a feature which has led to its application for pistons. In the wrought and heat-treated condition the alloy appears to resist corrosion much better than duralumin.

The " R.R." Alloys.

The light R.R. alloys have been developed by Messrs. Rolls-Royce, Ltd., and an excellent review of their properties has been given by Harvey-Bailey,* from whose paper the following information has been extracted.

Typical compositions and their designations are given in the following table:

	Copper.	Nickel.	Mag-nesium.	Iron.	Titani-um.	Silicon.	Purposes for which the Alloys are used.
R.R. 50	1·30	1·30	0·10	1·00	0·18	2·20	General casting purposes.
R.R. 53	2·25	1·30	1·60	1·40	0·10	1·25	Die-cast pistons.
R.R. 56	2·00	1·30	0·80	1·40	0·10	0·70	Alloy for forged work.
R.R. 59	2·25	1·30	1·60	1·40	0·10	0·50	Forged pistons.

' *The Nickel Bulletin*, Vol. III, No. 8, Aug., 1930.

It will be noted that the copper contents are considerably lower than those of either duralumin or Y alloy. All the alloys contain nickel, and the proportions of iron are much greater than in most light aluminium alloys, whilst the use of ferro-titanium as a cleansing and deoxidizing agent is noteworthy.

As might be anticipated from their compositions, all the R.R. alloys are susceptible to heat-treatment, and their properties are considerably improved thereby. With the exception of R.R. 50, the treatment consists in soaking for 2–4 hours between 510° and 535° C., and then quenching in water. The material is soft after quenching, but, unlike duralumin and Y alloy, the soft quenched material is comparatively stable, a property which is obviously advantageous since it permits of straightening and machining in the final stages of manufacture. Ageing is carried out by tempering at 155°–175° C. for about twenty hours.

The mechanical properties of R.R. alloys are as follows:

	Proof Stress.*	Y.P.	M.S.	Elonga-tion.	Reduction of Area.	Brinell No.
R.R. 50—as cast	7	8	14–15	7–10	12	72
R.R. 50 — heat-treated ..	12–14	14	16	4–8	10	80
R.R. 53—as cast	12	13	14	3	4	80
R.R. 53 — heat-treated ..	22	23	23–25	1	1·5	132–152
R.R. 56 — heat-treated ..	23–25	24–27	28–32	10–20	14–25	121–160
R.R. 59 — heat-treated ..	19·2	21	24	8	17·8	127

The R.R. alloys have comparatively high tensile strengths at elevated temperature, a fact clearly shown by the following test results obtained by Harvey-Bailey on heat-treated specimens of the alloy R.R. 53:

Temperature ..	15° C.	150° C.	250° C.	300° C.	350° C.
M.S.—tons/sq. in.	24·0	22·5	19·5	14·0	8·0
Brinell number ..	138	127	68	52	—

Mean values for other important physical properties of the R.R. alloys are as follows:

Specific gravity, 2·70–2·75.
Thermal conductivity, 0·40 C.G.S. units.
Coefficient of linear expansion, 0·000022 per 1ᶜ C.

* The stress at which the stress-strain curve departs by o·1 per cent of the gauge length from the line of proportionality.

Aluminium-copper-zinc Alloys.

At one time aluminium-zinc alloys were extensively employed for crankcases, gear-boxes, and other light alloy castings.

Zinc is comparatively cheap, and the zinc-aluminium alloys have relatively low melting-points, with the consequence that they are easily melted and cast into very intricate shapes.

The addition of zinc to aluminium results in increased strength but lower ductility. An alloy containing about 13 per cent of zinc has a tensile strength of 10 tons per square inch, with an elongation of 15 per cent and a specific gravity of about 3.

Such a combination of physical properties is, of course, very useful, but, unfortunately, the alloy exhibits " hot-shortness " to a pronounced degree, and consequently cracks readily develop in the castings. It is chiefly on account of this defect that the straight Al-Zn alloy has been almost entirely superseded by an alloy containing 2·5 to 3 per cent of copper and 13 to 14 per cent of zinc, which is covered by the B.E.S.A. specification 2L5.

This alloy is now widely employed for gear-boxes, brake-shoes, crankcases, &c., and the castings have the following properties:

Density.	M.S., tons per sq. in.	Elongation, per cent.	Brinell No.
3·0	11—16	4—10	60—70

Chill castings have the higher tensile strengths. 2L5 is a cheap useful alloy of fair strength and is easily machined, but does not offer any pronounced resistance to corroding influences.

Aluminium-silicon Alloys.

Since the specific gravity of silicon is lower than that of aluminium, alloys of the two are lighter than most other aluminium alloys, and it is this property which has made its greatest appeal in those instances in which lightness is of primary importance.

Of the alloys rich in silicon, the Air Ministry Specification D.T.D. 25 may be cited as being representative of the more useful types for casting purposes. This material has the following composition:

Silicon, 10·0—14·0 per cent.
Manganese, 0·5 per cent (max.).
Iron, 0·75 per cent (max.).
Aluminium, the remainder.

Aluminium and silicon give rise to the formation of a simple eutectiferous system exhibiting a limited degree of mutual solid solubility. The eutectic, which therefore consists of two solid solutions, freezes at 577° C., and contains rather less than 12 per cent of silicon. In consequence, the alloys covered by the above specification consist essentially of the eutectic, but may also contain either the primary silicon or the primary aluminium solid solution. Any slight variation in composition on either side of the eutectic does not appear to have any great influence on the physical properties of the cast alloys, however, and the following results may be considered as typical of the alloys containing between 10 and 14 per cent silicon:

Y.P., tons per sq. in.	M.S., tons per sq. in.	Elongation, per cent.	Density.
10–12	12–14	7·0—8·0	2·60–2·70

Of the aluminium alloys these are among the most resistant to corroding influences, and on this account find considerable application for marine purposes where a light alloy is desired. Iron is kept as low as possible, since it impairs both ductility and corrosion-resistance. The alloys retain their strengths very well at moderately high temperatures, a property which renders them suitable for the moving parts of internal-combustion engines.

A high degree of fluidity is readily obtained with these alloys, and shrinkage during solidification is much less than in most other light aluminium alloys. These factors lead to the production of sound castings of intricate and varying section, free from cracks.

The castings are dense and non-porous, and will withstand fluid pressure without leakage.

The properties of the aluminium-silicon alloys are considerably improved by a patent process known as " modification ". This consists in treating the molten alloy with one or other " modifying agents " just before casting. The materials employed, which are all covered by patents, include the alkali metals sodium and potassium, their hydroxides and fluorides, and the alkaline earth metals, such as calcium. The function of the modifying agent is not yet fully understood, but the treatment results in a remarkable refinement of the structure of the eutectic, with a consequent improvement in the physical properties, as will be evident from the following results on a modified 11 per cent silicon alloy:

Y.P., tons per sq. in.	M.S., tons per sq. in.	Elongation, per cent.	Brinell No.
7	14	14	62

It is a matter of interest that the modification apparently alters the composition of the eutectic to about 15 per cent of silicon, and its freezing-point is about 15° C. lower than that of the normal eutectic.

Aluminium silicon alloys of this type have a wide application, and are employed for sliding panel doors, petrol pumps, general shipwork, and die and pressure castings for motor-cars and aircraft.

Alloys of much lower silicon content (2–3 per cent) and containing about 4 per cent of copper are of comparatively recent development. An alloy of this type has been developed in Germany under the name of " Lautal " which can be employed in both the cast and wrought states. This material promises to become a very serious rival of both Y alloy and duralumin.

The best properties are only induced in Lautal by subjecting it to a heat-treatment similar to that employed for duralumin. Typical test results are as follows:

	Y.P., tons per sq. in.	M.S., tons per sq. in.	Elongation, per cent.	Brinell No.
As cast	6	11	10	59
Heat-treated	10	18	9	95

The density of Lautal is about 2·75.

Alloys of Magnesium and Aluminium.

Magnesium is one of the lightest of metals and has a specific gravity about two-thirds of that of aluminium. It is the extreme lightness of magnesium and its alloys which has made its greatest appeal to aircraft and automobile engineers, since it permits of the production of maximum power with minimum weight.

Pure magnesium, like aluminium, is a weak metal, and in the cast state has a tensile strength of about 7 tons per square inch only; although the strength may be raised to about 12 tons per square inch by rolling. The coefficients of expansion of magnesium and its most important alloys are about the same as those of the light aluminium alloys, but their thermal conductivities are distinctly inferior, the values for the pure metals being 0·38 and 0·5 C.G.S. units respectively.

The most important magnesium alloys, which include the well-known and widely employed " Electron " alloys, are those containing aluminium with or without zinc, and smaller proportions of manganese, silicon, and cadmium.

The magnesium alloys do not exhibit any pronounced corrosion-

resisting properties, although some improvement is obtained by the introduction of manganese. Too great a proportion of manganese may seriously impair the other physical properties of the alloy, however, and the element must be kept within definite specification limits.

Magnesium alloys are employed in both the cast and wrought states. For castings, the aluminium content is rather lower and the zinc content higher than in the alloys intended for forgings.

The Air Ministry specifications for compositions and minimum test values are given in the following table:

	Al.	Zn.	Mn.	Si.	Cd.	S.G.	M.S.	Elongation, per cent.	Brinell No.
D.T.D. 59	3.5–6.5	2.5–3.5	0.25–0.70	—	—	1.8–1.83	12	6	—
D.T.D. 88A	$10.0_{max.}$	$1.5_{max.}$	$1.0_{max.}$	—	—	1.82	15	5	45
D.T.D. 90	$8.0_{max.}$	—	$1.0_{max.}$	$2.5_{max.}$	$1.5_{max.}$	—	16	4	60

The alloy D.T.D. 59 is a casting alloy used for crankcases, &c., whilst the alloys D.T.D. 88A and 90 are used for forgings and stampings.

Alloy D.T.D. 90 is suitable for pistons, but D.T.D. 88A is not regarded as satisfactory for this purpose. Both these alloys are now being employed for propellers.

All the magnesium alloys are easily machined. Very fine turnings or borings may take fire during machining, however, and for this reason it is advisable to employ a rather heavier cut in order to reduce the possibility of ignition to a minimum.

Miscellaneous Non-ferrous Metals and Alloys

Nickel.

Commercially pure nickel, in the forms generally supplied to the iron, steel, and non-ferrous metal founders for alloying, is unsuitable for any engineering purpose. This is due to the fact that the metal is liable to contain appreciable amounts of either carbon or nickel oxide. The latter embrittles the metal, whilst carbon in the form of graphite impairs its mechanical properties, reduces its resistance to corrosion, and imparts a poor finish to the surfaces of polished work.

If the metal is remelted and its carbon content kept very low, the addition of a small proportion of a deoxidant, such as magnesium or manganese, just before casting results in the production of a

material which may be readily worked either hot or cold.   The product, which may then contain up to 0·5 per cent of impurities, is known as malleable nickel, and is now extensively employed in both the cast and wrought states.   The best forging and rolling temperature range is 1100°–1200° C.   Average test results are as follows: *

	Y.P.	M.S.	Elongation, per cent.	Reduction of Area, per cent.	Brinell No.
As cast	9·0–13·0	27·0–31·0	15–35	30–50	80–100
Cold-rolled	45	63	—	—	150
Rolled and annealed ..	9–13	29–33	43–53	65–75	75–95

The material is softened and obtained in the best condition for further cold-work by annealing between 600° and 800° C.

Malleable nickel resists attack by organic and dilute mineral acids, and, in particular, the action of caustic alkalis, ammonia, and salt solutions.   The material thus finds considerable application in chemical engineering for agitators, auto-claves, tank-linings, pumps, and valves for the production of caustic alkalis, &c., and in the handling equipment of foodstuffs.

Nickel has a fine white colour and will take a brilliant finish, and on this account is extensively employed for decorative purposes and in cafeteria work.

Other important physical properties of nickel are as follows:

Specific resistance = 10·2 microhms per cm.³.
Temperature coefficient of resistance = 0·005 per 1° C.
Coefficient of linear expansion = 0·0000129.

The electrical properties of nickel exhibit a pronounced alteration at a temperature between 370° and 380° C., due to a transformation analogous to that of the α-β change in iron. α nickel, which is the stable form below 370° C., has about one-third of the permeability of α iron, whereas β nickel is non-magnetic.

The thermal conductivity of nickel varies with temperature, as will be evident from the following data, due to Schofield: †

Temperature.	Thermal Conductivity.		
100° C.	0·145 C.G.S. units		
290° C.	0·128	,,	,,
490° C.	0·128	,,	,,
733° C.	0·147	,,	,,

These values suggest the occurrence of a minimum corresponding with the α-β change.

* P. D. Merica, *Amer. Soc. Steel Treating Handbook*, 1928.   † *Proc. Royal Soc.*, 1925, Vol. CVII.

Alloys of Nickel and Chromium.

Nickel and chromium are mutually soluble in the solid state, and the resulting solid solutions possess entirely different properties from those of either of the constituent metals. The alloys are characterized by their high electrical resistivities, resistance to attack by hot acids and alkalis, and resistance to oxidation at very high temperatures.

Nickel-chromium alloys are employed in both the cast and wrought states. In the cast condition the tensile strength is between 20 and 30 tons per square inch. Working considerably improves both strength and ductility, and the alloys retain their strengths quite well at elevated temperatures. The straight nickel-chromium alloys are not easy to make, and their initial cost is rather high. For these reasons, particularly for castings, part of the nickel is often replaced by iron, whilst in some instances this substitution, which may amount to as much as 25 per cent, is at the expense of both the nickel and the chromium. A typical casting alloy has the following percentage composition:

Nickel, 61·2; Chromium, 19·7; Silicon, 1·94; Manganese, 0·86; Carbon, 0·62; Iron, 15·3.

Such materials resist oxidation and scaling at temperatures below 1100° C., and are employed for annealing and case-carburizing boxes, pyrometer protecting sheaths, muffle furnace linings, resistor elements of heat-treatment furnaces, oil-fuel nozzles, nozzles in glass bottle-making machines, Diesel engine valves, valves of the "mushroom" type, such as those used in gas-producer systems, &c.

In the form of rolled and drawn wire and tape, the nickel-chromium and the nickel-chromium-iron alloys, known as *nichromes*, are widely employed for electrical heating equipment. As windings for electric furnaces these materials are invaluable, owing to their high electrical resistivities and low temperature coefficients, since these properties permit of the easy attainment and maintenance of almost any desired temperature.

The best types of wire for this purpose contain about 80 per cent of nickel and 20 per cent of chromium, but, unfortunately, their initial cost is high. The nickel-chromium-iron alloys are cheaper, but may not be used continuously at temperatures above 850° C. The more important physical properties of these materials are as follows:

Nickel, per cent.	Chromium, per cent.	Iron, per cent.	Resistivity. Microhms per cm.³.	Temperature Coefficient.	Maximum Temperature suitable.	Coefficient of Linear Expansion.
80	20	—	105–110	0·000098	1150° C.	0·000015
85	15	—	90–95	0·000254	1000° C.	0·000015
65	10	25	95–105	0·000210	825° C.	0·000012

The maximum temperatures at which these materials may be used depends somewhat on the cross-sectional area of the wire or tape, and the values given in the above table will thus only serve as a general indication. Thicker wires withstand prolonged heating at very high temperatures better than those having a much smaller diameter. On the other hand, thin wires may be bent and twisted more readily, and on this account are generally preferred for furnace windings, since the attachment of the ends of the winding to the connecting terminals is a simpler matter than if thicker wires were employed.

Nickel-chromium alloys of different compositions are also employed as thermocouple wires in high temperature work.

Bearing Metals—White Metal " Anti-friction " Alloys.

Pure metals and alloys consisting entirely of one solid solution are unsuitable for use as bearings. Alloys of two or more metals are employed for this purpose, and their microstructures show at least two constituents.

The chemical compositions of bearing alloys vary widely, and are dependent to some extent on the conditions of load and speed involved. Generally, however, there is always one object in view, i.e. the production of an alloy consisting of hard particles embedded in a softer matrix. The function of the hard constituent is to resist wear and provide a surface with a low coefficient of friction, whilst the soft matrix allows the bearing to adjust itself to the journal, thus tending to yield even distribution of the load and prevent local heating and seizing.

In use, the hard particles stand out in slight relief, the softer matrix wearing to yield a series of microscopic channels which form an effective irrigation system for the lubricant.

For obvious reasons the melting-point of a bearing alloy must not be too low.

The metals employed are copper, tin, lead, and antimony. Alloys containing high proportions of zinc have been employed for railway work in the past, but the results have not been altogether satisfactory, since the zinc induces a tendency to seizing. Good

results are possible with the binary alloys, copper-tin, antimony-tin, and lead-antimony, but the ternary alloys, copper-tin-lead, copper-tin-antimony, copper-antimony-lead, and tin-antimony-lead, yield better results.

The copper-tin alloys known as the bearing bronzes have already been considered. In the phosphor-bronzes the copper-copper-phosphide eutectic is the hard constituent, and in the ordinary bearing bronzes the α-δ eutectoid serves the same purpose.

In all cases there is a more or less optimum size for the hard particles. If too large, the hard parts tend to chip out, whilst if too small, the alloy approximates to a pure metal in so far as its properties as a bearing alloy are concerned, and effective lubrication is not obtained. The hard particles should also be uniformly distributed in the softer matrix. The two factors which exert the greatest influence on the size and distribution of these hard particles are: (i) the temperature at which the alloy is cast, and (ii) its rate of cooling after casting. These influences are more fully considered in a subsequent section.

White-metal Alloys.

Antimony is a constituent of most anti-friction alloys, and may be present in almost any proportion up to about 15 per cent. With higher proportions the alloys become too brittle.

The white-metal bearing alloys fall into one of two classes having either a lead or a tin base. The tin-base alloys are known as *Babbitt metals*, the name embracing quite a considerable range of compositions.

Apart from antimony, therefore, the essential constituents of white-metal bearing alloys are either tin or lead. The binary systems involved are therefore worthy of some consideration, and are given in figs. 184 and 185. In both instances, the antimony gives rise to the hard constituent—the γ solid solution in the antimony-tin system, and practically pure antimony in the lead-antimony system. Both constituents crystallize in forms approximating to cubes. These "cuboids" are relatively light, and if sufficient time is allowed, as when the cast alloy is slowly cooled, flotation occurs and the hard particles segregate in the upper part of the casting. The structure of such an alloy is shown in fig. 186 (facing p. 266). This certainly represents a somewhat extreme case, but serves to reveal to what extent this flotation is possible.

Flotation may be minimized by (*a*) fairly rapid cooling, or (*b*)

by the introduction of a third metal, such as copper or nickel, which combines with one of the original constituents to yield an
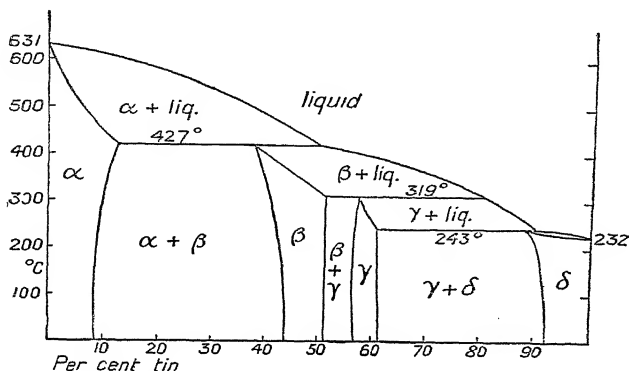
Fig. 184.—Equilibrium Diagram: Antimony-tin Alloys

alloy possessing a much higher freezing-point than that at which the cuboids first crystallize. This constituent freezes first and forms
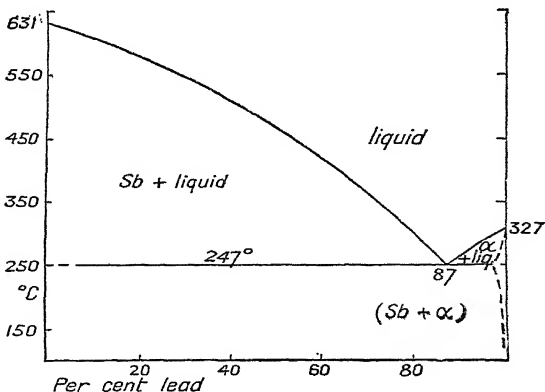
Fig. 185.—Equilibrium Diagram: Antimony-lead Alloys

a network throughout the molten mass. Flotation is thus inhibited by the entrapping of the cuboids as they form at lower temperatures.

METALLURGY

In a very comprehensive paper on white-metal alloys, Mundey, Bissett, and Cartland * give the typical compositions, properties, and applications shown opposite.

According to Sir H. Fowler,† the Association of Railway Locomotive Engineers decided to adopt the following alloys, which have proved satisfactory for many years, as temporary standards:

	Tin.	Antimony.	Copper.	Lead.	Brinell No. (500 Kgm.)
No. 1	85	10	5	—	33
No. 2	60	10	2	28	20
No. 3	12	13	—	75	19

The first two are considered as being satisfactory to meet all cases of bearings subjected to hammering or repetition stresses, whilst the lead-base alloy No. 3 is suitable for the more lightly loaded bearings in which the journal or shaft only rotates.

With two exceptions, all the above alloys contain antimony, copper, and tin, and their microstructures would show reticulations of the copper - tin compound with the hard antimony constituent embedded in a matrix of either the tin-rich or the lead-rich alloy.
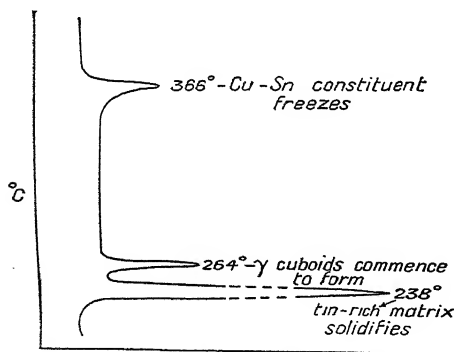
Fig. 187.—Inverse-rate Curve of Antimony-copper-tin bearing Alloy

The precise form in which the copper-tin constituent exists exerts a considerable influence on the properties of the alloy, and is governed by the casting temperature and the conditions of cooling. A typical cooling curve for a tin-base bearing alloy is given in fig. 187. In view of the fact that these alloys are readily obtained in a condition of complete fluidity, the general tendency in practice is to heat them to much higher temperatures than are necessary; and if an alloy is not allowed to cool before casting, its final properties may be altogether unsatisfactory.

* *Journ. Inst. Met.*, 1922, No. 2.   † *Journ. Inst. Met.*, 1924, No. 1.

Fig. 186.—Bearing alloy containing 15 per cent
antimony, 85 per cent tin, after very slow
cooling from a high temperature. Shows
excessive flotation of the γ cubes (white). × 20.
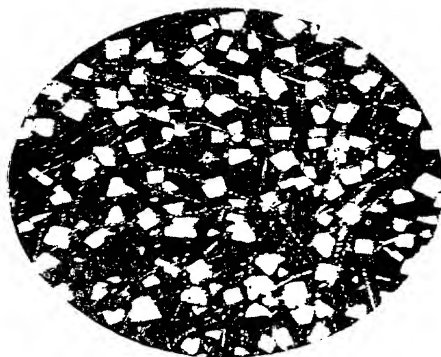
Fig. 188.—Bearing alloy: 82 per cent tin, 14
per cent antimony, 4 per cent copper. γ cubes
(white) and copper-tin constituent in tin-rich
matrix (black)—good structure. × 50.

Composition				Tensile Properties		Compression Test Values		Brinell Number (500 Kgm. Load).	Remarks.
Tin.	Antimony.	Copper.	Lead.	Maximum Stress.	Elongation.	Yield-point.*	Load (tons per sq. in.) required to compress Piece to Half-length.		
93·0	3·5	3·5	—	5·12	11·6	3·569	14·732	24·9	Combines maximum toughness with strength—probably ideal for big-end bearings.
86·0	10·5	3·5	—	6·65	7·1	4·372	17·232	33·3	Harder than the above but still tough—very useful for general work for main bearings.
83·0	10·5	2·5	4·0	5·60	Nil	4·284	17·640	34·5	Although the lead reduces the elongation to nil, the alloy has excellent shock-resisting properties.
80·0	11·0	3·0	6·0	5·70	Nil	4·640	17·500	32·1	Very useful for heavy loads and high speeds: Diesel engines, turbines, rolling-mills, locomotives.
60·0	10·0	1·5	28·5	5·04	Nil	3·696	12·856	27·1	For internal-combustion engines of all types, steam-engines, dynamos, locomotives, &c.
40·0	10·0	1·5	48·5	4·58	Nil	3·660	11·284	21·8	Generally useful for heavy pressure and medium speed or medium pressure and high speed: automobile engines, railway and tramway bearings.
20·0	15·0	1·5	63·5	5·48	Nil	4·016	12·212	31·3	Also useful for medium pressures and speed or light pressure and high speed.
78·0	11·0	11·0	—	6·36	Nil	4·550	17·856	37·0	"Plastic" metal—has a long range of solidification and used very extensively by millwrights and marine engineers for repair work; hard and durable and self-tinning.
5·0	15·0	—	80·0	4·69	2·8	3·590	13·356	24·9	"Magnolia" metal type—capable of carrying their load and continuing their duty under increased temperatures to a greater extent than many tin-base bearing metals in similar circumstances.

* Yield-point taken as the load (in tons per square inch) which produced 0·001″ permanent deformation—original length of test-piece, 0·564″.

Heyn and Bauer * investigated the effects of casting conditions on an alloy having the following composition: tin, 86·43 per cent; antimony, 8·76 per cent; copper, 4·51 per cent; and their conclusions are embodied in the following table:

Conditions.	Microstructural Characteristics.
Low casting temperature (400° C.) and rapid cooling.	Small γ cubes and Cu-Sn constituent in needles.
High casting temperature (700° C.) and rapid cooling.	Small γ cubes and Cu-Sn constituent in chains of crystallites.
Low casting temperature (400° C.) and slow cooling.	Large cubes and Cu-Sn constituent in star-like masses.
High casting temperature (700° C.) and slow cooling.	Large cubes and chain-like aggregates for the Cu-Sn constituent.

Large cubes with the copper-tin constituent in the form of needles are to be avoided, and Heyn and Bauer advise a casting temperature not too high combined with a moderate rate of cooling. The latter is controlled by casting the alloy into a warm mould or bearing, preheated to a temperature between 100° and 200° C.

The microstructure of a typical tin-base bearing alloy is shown in fig. 188 (facing p. 266).

The copper-antimony-lead alloys should be cooled rather quickly so as to distribute the lead as uniformly as possible.

Solders and other Fusible Alloys.

Plumber's solder consists of two parts of lead and one part of tin. This alloy begins to freeze at about 240° C., but solidification is not complete until the eutectic temperature (180° C.) is reached. It is this long range of solidification which enables the plumber to make his well-known " wiped " joint. Tinman's solder, which is employed for general purposes, consists of two parts tin and one part lead, and has almost eutectic composition. This alloy is therefore easily melted, and solidifies very quickly after it has been applied.

Ternary and quaternary alloys can be made with any desired melting-point from about 60° C. upwards. The best-known of these " fusible metals " are " Rose's metal ", containing 2 parts bismuth, 1 part each of lead and tin, with a melting-point of 93·7° C., and " Wood's metal ", which melts at 60·5° C. and consists of 4 parts bismuth, 2 parts lead, 1 part tin, and 1 part cadmium.

Fusible alloys containing lead as the principal constituent are employed for electrical fuse wires.

* *Stahl und Eisen*, 1911, **13**, 509.

Pure lead and pure tin are employed as fusible plug fillings in boilers, and experience has shown that the most satisfactory results are obtained only by using metals of an exceptional degree of purity.

Note on the Preparation of Non-ferrous Microsections.

The preparation of non-ferrous metals for microscopic examination is carried out, excepting for the final polishing, in a manner similar to that employed for ferrous specimens. In order to obtain a satisfactory surface the final polishing is done by hand, the specimen being rubbed backwards and forwards on Selvyt cloth impregnated with metal polish until the scratches disappear. A thin film of grease invariably remains on the surface, and if it is not removed, a dirty and unevenly etched surface is obtained The specimen should therefore be cleaned by rubbing with a piece of clean cotton-wool, previously wetted and rubbed on soap.

Etching Media.—The more important etching reagents which have been employed in the preparation of the microsections illustrated in the preceding pages are given below. In every instance, after etching, the etching reagent must be completely removed by washing the specimen in running water. The surface is then dried by means of alcohol.

Brasses are etched by gently rubbing the polished surface with a piece of cotton-wool (held in a pair of brass crucible tongs) impregnated with a solution of copper sulphate and ammonia. This reagent is the one most favoured by the author and his colleagues, although a 10 per cent solution of ammonium persulphate in water containing about 20 per cent of ammonia yields equally satisfactory results.

The most satisfactory etching reagent for the bronzes is an acidified solution of ferric chloride. This is made up of equal volumes of water and concentrated hydrochloric acid, concentrated ferric chloride solution then being added until the mixture has a rich golden-yellow colour. This reagent is one of great utility, and will often yield satisfactory results when others fail to do so. It may be used for all the copper alloys, including the aluminium bronzes, and also yields admirable results for the stainless and austenitic steels.

Several reagents may be employed for the etching of the light aluminium alloys, but a 20 per cent solution of nitric acid in water at 70° C. yields very satisfactory results. After etching, the silicon

constituent has a bluish-grey colour, whilst the $CuAl_2$ appears dark-brown or black.

A cold 10 per cent solution of hydrochloric or nitric acid forms a satisfactory etching medium for the white-metal bearing alloys.

The Welding of Metals

The art of joining metals must have been practised since very remote times. Primitive methods produced metals in small masses, and the demand for larger pieces could not be met by any other method than welding. It is only comparatively recently, however, that this and related branches of metallurgical engineering have been considered from a scientific aspect.

The joining of two or more pieces of metal is a problem which often arises to-day, notably in connexion with repair work in ship-building, automobile and chemical engineering.

Metals may be joined by soldering, brazing, or welding. The three methods do not differ very much in principle, although the terminology is rather confusing. The term welding originally comprised the union of parts at a temperature below the melting-point of the material, as, for instance, in the making of the black-smith's weld for wrought iron. The term is now also applied to those processes in which a part of the metal to be joined or a separate piece of metal is actually melted.

Since the processes involve the heating of parts, the materials become coated with a film of oxide which would inhibit the metal-to-metal contact. To remove this coating a flux is employed. The flux must be capable of melting at a temperature considerably below that at which the actual joining of parts takes place, and at this temperature must take into solution the oxide or oxides involved whilst still remaining sufficiently liquid to be expressed. On the other hand, the metals or alloys used in effecting the juncture must be capable of forming solid solutions with the metals to be joined.

Soldering.

" Soft " soldering is generally employed for the union of thin pieces of material, generally mild steel sheet, where air-tight or water-tight joints are required and the strength of the joint is of minor importance. A low melting-point alloy is employed as a solder, but since its strength is generally lower than that of the

metal, the section is made thicker in the vicinity of the actual joint. Even when the advantage of the increased thickness is taken into consideration, however, the process is unsuitable for stressed parts.

The flux usually employed in soldering is chloride of zinc, obtained by " killing " commercial hydrochloric acid by the addition of metallic zinc until the solution has practically no further action on the metal. The flux, which contains free acid, cleans the metal, and the zinc chloride dissolves any thin oxide films which may remain. The compositions of solders have been indicated on p. 268.

Brazing.

The process of brazing is really a soldering operation, but the material used for cementing the parts together possesses a fairly high melting-point and considerable strength. This process is particularly suitable for the joining of brass, but is also often applied to iron and steel, bronze, and other non-ferrous alloys.

As the term suggests, brazing alloys are essentially brasses, i.e. alloys of copper and zinc, the compositions of which have been indicated on p. 218. The better qualities contain notable proportions of silver. Silver solder has a somewhat lower melting-point than ordinary brazing brass. Copper-nickel-zinc alloys are also employed for brazing, typical compositions having been given on p. 242.

Brazing alloys are generally melted by means of an ordinary gas blowpipe.

Welding.

In all welding operations a suitable flux should be employed if the best results are to be obtained. The functions of the flux are as follows: (a) it shields the metal from atmospheric oxidation, (b) forms a readily fusible substance (slag) with oxide already present or oxide formed during the actual welding process, and (c) tends to minimize volatilization of important constituents in the metal to be welded. The selection of a suitable flux constitutes one of the greatest problems in welding, and its composition must be varied to suit the particular metal or alloy to be joined.

The coefficients of expansion and the thermal conductivities of the materials involved must be taken into consideration. In general, the expansibilities are high and, therefore, the volume changes

which occur during heating and cooling are considerable. For this reason, the material should not be held too rigidly during welding or subsequent cooling, since internal stresses are thus developed and cracks may be formed. After being welded, the articles should not be cooled too rapidly.

The thermal conductivity, which differs greatly in different metals, exerts an important influence in welding. Thus a high conductivity metal such as copper must be subjected to a preliminary heating in parts somewhat remote from the weld. This aids the actual welding, and also prevents rapid cooling of the weld due to the transference of heat by conduction.

Several methods of welding are employed. As already indicated, true welding consists in the adhesion of parts at a temperature below the melting-point of the material, a method often applied to iron, mild steel, and the noble metals such as platinum.

" Thermit " welding is still used in the case of heavy iron and mild steel parts. Thermit powder, consisting of an intimate mixture of powdered aluminium and oxide of iron, is placed over the parts to be joined. The mixture is then fired, and the iron is reduced to the metallic state. The heats of formation of ferric oxide and aluminium oxide are 195,600 and 392,600 calories respectively. Thermochemically, therefore, the reduction of ferric oxide by aluminium is represented as follows:

$$2Al + Fe_2O_3 = Al_2O_3 + 2Fe + 197,000 \text{ cal.}$$
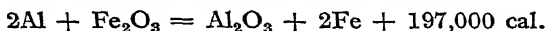
The reaction is thus highly exothermic, and the heat liberated suffices to retain the reduced iron in a perfectly fluid state.

Both resistance and arc methods are employed in electrical welding. In the former method the metal in the vicinity of the weld is made part of an electrical circuit, the heat then generated during the time the current is maintained being sufficient to render the material plastic and enable adjacent parts to adhere together. The pieces to be joined are clamped between heavy copper electrodes or carbon blocks. Resistance welding is only applicable for the joining of parts of comparatively small cross-section, and for " spot " welding, where the weld is not continuous, the material being joined in several places only. Spot-welding is particularly useful for temporary joints in such instances as the joining of sheets which are to be subjected to continuous heat-treatment processes, &c

Arc-welding, in which metal electrodes of definite composition are employed, is now of very wide application. A suitable flux

must be employed, otherwise, owing to the intense heat of the arc, excessive oxidation and volatilization occur. Recently, flux-coated electrodes which yield automatic deposition of the flux on the weld as melting proceeds have been strongly advocated.

In a very interesting article on flux-coated electrodes, Lacy * describes the use of coated electrodes in which special elements are incorporated in the flux. During welding, these elements find their way into the metal of the weld and increase its strength by counteracting volatilization and oxidation losses. By this means it is also possible to deposit alloy steels on the surface of ordinary mild steel.

Autogenous welding is usually understood to imply the use of the oxy-acetylene or oxy-water-gas blowpipe, although, apart from the means of heating, the same principle is employed in arc-welding.

In autogenous welding methods, welding-rods are employed having a composition similar to that of the material to be welded, although the welding-rod is generally somewhat richer in the elements subject to volatilization.

In oxy-acetylene welding correct proportions of oxygen and acetylene are necessary to secure the best results. With a blowpipe flame rich in oxygen the weld is liable to contain abnormal amounts of oxide even when a proper flux is used. On the other hand, too great a proportion of acetylene may result in a pronounced carburizing action on welded iron and steel joints, brittle high-carbon welds being obtained in consequence.

Recently, very successful results have been obtained in welding by means of the atomic-hydrogen torch. A stream of hydrogen is passed between the poles of an arc with tungsten electrodes. The hydrogen is dissociated into atoms, and when these impinge on the metal to be joined, association into molecules occurs with the liberation of heat. By this means an intense and extremely localized source of heat is possible. An excellent account of the welding of ferrous and non-ferrous materials by the atomic-hydrogen flame has been given by R. A. Weinmain.†

It is often claimed that the properties of a weld are just as perfect as those of the unwelded material. Excepting those instances in which the composition of the welding-rod is different from that of the welded material, the properties of a weld are

never quite so good as those of the main mass, and, indeed, this cannot be expected. Even in true welding where the temperature is well below its melting-point the material is grossly overheated, whilst in autogenous welding the material of the actual weld is in the cast state. In both instances the weld may be toughened considerably by hammering whilst it is still at a red heat, with reheating if necessary. The properties of the weld may still further be improved by subjecting the material to a normalizing treatment.

In some cases, such as with tee-pieces, &c., hammering is not permissible, and one can then only rely on a process of heat-treatment to improve the mechanical properties of the welded parts. Wherever possible a final normalizing treatment should always be given, since this not only improves the ductility of the weld itself, but also tends to obliterate the coarse brittle overheated structure on either side of it. Further, during the reheating for normalizing diffusion occurs, and a more homogeneous material obtained.

The only really satisfactory means of determining the properties of a weld is by the aid of the microscope.

The Welding of Iron and Steel.

Wrought iron can be welded without difficulty, but, as indicated on p. 146, the higher carbon steels are not so tractable. Mild steel may be welded almost as readily as wrought iron.

The welding of iron and mild steel in the ordinary blacksmith's hearth is apparently a simple operation requiring little skill, but if the greatest care is not exercised, the ductility of the weld may not be so satisfactory as is desirable. If the ends to be welded are kept in the oxidizing part of the fire for too long a period, the weld is liable to contain much oxide of iron and slag, and therefore be brittle. On the other hand, prolonged heating in contact with the coke may result in a weld rich in carbon and sulphur.

The blacksmith uses sand as a flux. The silica in the sand combines with any oxide of iron formed to yield a readily fusible slag which can then be expressed by hammering. To facilitate this last feature the surfaces to be welded are made convex.

Greater uniformity is obtained with autogenous welding, but a final normalizing treatment from about 900° C. should not be omitted.

In general, alloy steels cannot be said to yield satisfactory welds. One notable exception, however, is stainless steel and its

allied products, the austenitic nickel-chromium steels. The Air Ministry specification for the austenitic non-corrosive welding-rods is as follows:

Carbon, 0·25–0·55 per cent; Chromium, 15·5–19 per cent; Nickel, 24–28 per cent; Silicon, 2–3·5 per cent; Manganese, 0·6–1·25 per cent; Iron, the remainder.

It is a well-known fact that the heating of alloy steels of the 18 per cent chromium, 8 per cent nickel type in the range 650°–900° C. greatly decreases their corrosion resistance, a consequence of the deposition of complex carbides at the crystal boundaries. This phenomenon is known as *weld-decay*. It will be obvious that some part of a welded article remote from the weld must be heated to a temperature within this range during the welding operation. Normalizing the welded article from above 1050° C. would certainly overcome any difficulty, but certain cases arise in which this treatment is neither possible nor desirable, and it is of interest to learn that several firms of steel-makers have, by slight alterations in chemical composition, notably the introduction of small proportions of tungsten and molybdenum, produced steels which are free from this defect. A useful test has been devised to reveal the susceptibility of these austenitic steels to a lowering of their corrosion resistance, after being heated to temperatures within the above range. The details of this test, as described in the Air Ministry specifications, are as follows: test-pieces are immersed for 72 hours in a boiling solution containing 111 grams copper sulphate and 98 grams (about 54 c.c.) strong sulphuric acid made up to 1 litre with water, precautions being taken to avoid concentration of the solution due to evaporation. The specimens are cleaned and subsequently subjected to a bend test, when inferior samples show a series of transverse cracks, and the steel is brittle. The method is really the analogue of the mercurous nitrate treatment for the detection of season cracking in brass.

Grey cast iron can be welded satisfactorily by autogenous methods, provided that a proper welding-rod is employed. In almost all cases a grey iron weld is desired, and the welding-rods are therefore specially prepared from irons rich in silicon but low in manganese. Cast iron must be very slowly cooled after welding. A suitable flux, commercially obtainable, consists of a mixture of sodium carbonate with about 10 per cent of borax and 5 per cent of pure white sand.

Welding of Copper and its Alloys.

A mixture of about equal parts of ordinary common salt, borax, and boracic acid is recommended as a suitable flux for the welding of copper and its alloys.

The welding of pure copper is not a simple matter. In view of its high thermal conductivity and the consequent rapid transference of heat away from the weld, it becomes necessary to preheat the metal to a high temperature before any attempt is made at welding. If badly oxidized the weld may be brittle, owing to the presence of the copper-copper-oxide eutectic at the boundaries of the copper crystals. Molten copper also absorbs acetylene and other gases resulting from its partial combustion, and the liberation of these gases during cooling forms blow-holes in the weld. These difficulties are largely overcome by using welding-rods containing small proportions of phosphorus and aluminium. After welding the metal should be mechanically worked, and finally normalized from a temperature not exceeding 600° C.

Brasses are welded more readily than copper, although a preliminary heating before welding is advisable. The greatest difficulty encountered in the welding of brass is due to volatilization of the zinc, clouds of the oxide fumes being evolved in the absence of a proper flux. Welding-rods containing a small proportion of aluminium yield the best results. The aluminium acts as a de-oxidant, prevents the formation of very small blow-holes or " pinholes ", and also tends to minimize volatilization. It is important to use a welding-rod of a composition similar to that of the brass to be joined. Thus, satisfactory results cannot be expected if a welding-rod of the " 70–30 " brass type is employed for the union of " 60–40 " brass parts.

The mechanical properties of the weld are improved by hammering. With a 60–40 brass this must be carried out at temperatures above 500° C., but mechanical work should only be applied to a 70–30 brass when the alloy is quite cold. In the latter case a normalizing or annealing treatment is almost imperative in order to destroy the hardness induced by cold-working.

. Bronze may be welded satisfactorily provided that the welding-rod has a composition approximating to that of the parts to be joined. Tin in bronze acts as its own deoxidant, but its reaction is somewhat violent, and may lead to the presence of blow-holes and much oxide of tin in the weld. These defects, together with

the loss of tin in the material itself, may yield a weak brittle weld. By using a bronze welding-rod of the appropriate composition, containing small amounts of phosphorus and aluminium, these difficulties largely disappear. Annealing of the weld directly after welding is advisable in most cases.

Welding of Aluminium and its Alloys.

The welding of aluminium and its alloys is extremely difficult owing to the rapid oxidation of the metal. Further, the oxide, when molten, has a greater density than the metal, and thus tends to sink into the weld. This seriously impairs the strength and corrosion resistance of the material, and on this account the welding of aircraft parts is prohibited, rivets being used instead. Aluminium also absorbs gases, and the liberation of these during solidification may yield a weld containing blow-holes, although, singularly enough, oxy-acetylene welding is considered as being more satisfactory than electric welding.

Aluminium and its alloys can be welded satisfactorily if a suitable flux and welding-rod are employed. The welding-rod should be pure aluminium, and this should be coated with the flux before welding is commenced. A flux consisting of 2 parts of borax with 1 part each of sodium and potassium chlorides gives satisfactory results. In some cases borax is dispensed with, the flux then consisting of the two chlorides with smaller proportions of potassium fluoride and potassium acid sulphate. The surfaces of the articles to be joined must be carefully cleaned beforehand if satisfactory results are to be obtained, and the alloys rich in aluminium should not be heated or cooled too rapidly. Aluminium bronzes can be welded, but better results are obtained by brazing with a brass containing about 20 per cent of zinc.

The aluminium-copper-zinc alloys, such as those used for crankcases, gear-boxes, &c., can be welded successfully if a welding-rod of similar composition is employed together with a proper flux. These alloys should be preheated, and slow cooling after welding is essential.

The copper-nickel alloys are easily welded, and satisfactory results obtained, provided that the oxy-acetylene mixture is not rich in sulphur.

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